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PYROLYSIS GAS CHROMATOGRAPHY AND
VARIABLE TEMPERATURE PYROLYZERS

by

(C) J. M. L. GRAY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies for acceptance,
a thesis entitled

PYROLYSIS GAS CHROMATOGRAPHY AND
VARIABLE TEMPERATURE PYROLYZERS

submitted by J. M. L. Gray in partial fulfilment of the
requirements for the degree of Master of Science.

ABSTRACT

Some parameters affecting the design and construction of pyrolysis units incorporating a temperature range are discussed. Two types of variable temperature range pyrolyzers were constructed. It was found that while the variable range pyrolyzers were more versatile, they were not as useful for the identification of an unknown compound by pyrolysis, as is an isothermal reactor. A temperature gradient reactor was found to be the most versatile reactor, and is suitable for use in a rapid PGC "poor man's mass spectrometer".

Two gold tubing reactors of different diameters were also constructed. The pyrolysis results that were obtained from operating the gold tubing isothermally were found to differ only slightly from those obtained in quartz tubing at the same extent of pyrolysis. However, it was noticed that the gold tubing required a higher temperature to result in the same extent of pyrolysis. This temperature difference is possibly due to kinetic effects of the wall of the tube, and the reaction conditions.

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PRINCIPAL SYMBOLS

D	Diffusion coefficient
F_{add}	Additive flow(rotameter reading)
F_m	Uncorrected flow rate measured at the outlet of system
F_m^0	F_m corrected to 0°C, 760 mm of mercury, and for the vapor pressure of water.
F_o	Flow rate at the entrance to the pyrolysis unit (0°C, 760 mm Hg)
F_p	Flow rate through the pyrolyzer corrected to the temperature and pressure in the pyrolyzer
F_{py}	Pyrolyzer flow (rotameter reading)
k	Rate constant of pyrolysis reaction
L	Length of pyrolysis zone, length of transition zone
p	Atmospheric pressure
p_{add}	Pressure due to additive flow (F_{add})
p_{py}	Pressure due to pyrolyzer flow (F_{py})
P_1	Pyrolysis tube one
P_2	Pyrolysis tube two
P_3	Pyrolysis tube three
P_4	Pyrolysis tube four
r	Radius of pyrolysis tube
R	Programming rate of gradient reactor
t	Time (general), time for thermal equilibration
t_p	Pyrolysis time
t_z	Transition time
T	Temperature (general)
T_i	Instantaneous temperature

T_o	Initial temperature, room temperature
T_p	Pyrolysis temperature
V_p	Volume of heated zone of pyrolyzer
α	Extent of pyrolysis
α'	Adjusted extent of reaction
τ	Residence time

PYROLYSIS GAS CHROMATOGRAPHY AND VARIABLE TEMPERATURE PYROLYZERS

1. INTRODUCTION

1.01 GENERAL BACKGROUND

The use of pyrolysis combined with gas chromatography (PGC) is an established technique in analytical chemistry (20). The technique has been used to examine a wide variety of materials -- both volatile and non-volatile.

PGC has been extensively reviewed (7, 18, 20, 24), and the authors of several recent books have discussed it (9, 15, 22, 26). Most of these articles have concentrated on the techniques and equipment associated with the pyrolysis of non-volatile substances such as polymers. However, the more recent reviews cover the advances in the pyrolysis of volatile materials also. Levy (20) reviewed the literature up to September 1965, and included such topics as reactor design and the reproducibility of fragmentation patterns for the pyrolysis of volatile materials.

Recently, the analysis of volatile materials by PGC has received increasing attention. Keulemans and Perry (17) investigated the cracking of several hydrocarbons in a quartz reactor. Sutton and Harris (28, 29) investigated the effect of several reactor parameters and suggested

optimum temperatures for the pyrolysis of several substances. Fanter, Walker, and Wolf (10) pyrolyzed several hydrocarbons in gold tubing and suggested a systematic method for the presentation of PGC data. The method that they suggest is to group the products of pyrolysis between stated intervals, according to retention index, and to report the normalized mole areas of the peaks found in each interval. The method of normalization is similar to the method used in reporting mass spectrometry data where the normalized peak heights are reported as a function of mass to charge ratios. At least two theses have been written on various aspects of PGC. Goforth (14) discusses reactor and equipment design for a rapid PGC system using a quartz reactor. Cramers (2) discusses some design considerations for a gold tubing reactor and the kinetics of pyrolysis reaction. He also gives pyrolysis data for several hydrocarbons.

1.02 REQUIREMENTS OF A PGC SYSTEM

Since the study of volatile materials by PGC is a new field, there is little agreement among the various workers on the optimum design of a pyrolysis system or even on standard conditions for pyrolysis. Thus the data accumulated by various workers can only be compared in a qualitative manner. The various systems differ so widely

that comparisons are often meaningless, since the fragmentation pattern is dependent on the reactor, and the various reaction parameters. Levy (21) describes the situation aptly:

"It becomes essential at this stage of development of PGC to focus our attention on those design features of pyrolysis units which control the course of the pyrolysis processes and provide the most desirable conditions for maximum interlaboratory reproducibility and correlation between the structure of pyrolysis materials and the composition of the products."

When a compound is pyrolyzed it is fragmented into several smaller, more volatile compounds that are usually simpler and more unsaturated than the parent compound. The fragmentation pattern is, ideally, characteristic of the structure of the parent; thus, indentifying the fragments should result in the indentification of the parent compound.

Because the fragments are usually volatile they are readily analyzed by gas chromatography, and the resultant pyrogram can be used to deduce the structure of the parent compound. A system such as that in Figure 1.01 can therefore be used to separate an unknown, and then to identify each peak from the first chromatograph by the combined pyrolysis-gas chromatograph of the second step (14).

Since the structural information obtained from such a system is similar to that obtained from mass spectroscopy, and since the system is much less expensive, PGC has been called "the poor man's mass spectrometer".

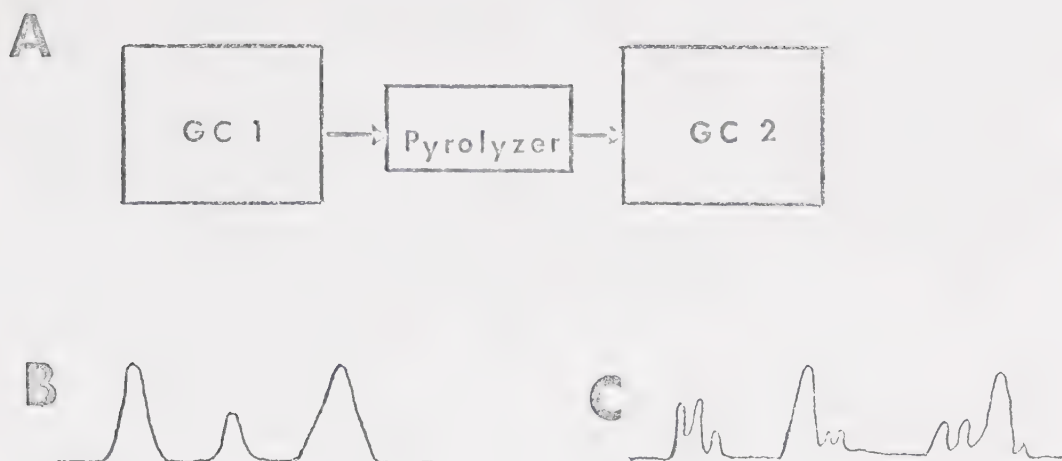


Figure 1.01 A PGC system for the separation and identification of an unknown compound. A. Block diagram of the system. B. Recorder output of GC 1. C. Recorder output of GC 2. From Goforth (14)

In practice, the pyrogram is seldom easy to interpret in an absolute manner, since factors such as reactor temperature and the time the sample spends in the pyrolysis zone can change the product distribution considerably. However, even when rigorous correlation between the identity of the fragments and the structure of the parent compound cannot be made, the fragmentation pattern gives a "fingerprint" of the parent which can be used for identification by comparison, using a file of fingerprints obtained from known compounds.

Since the fragmentation pattern depends on the reaction conditions, most studies of PGC have stressed the need for accurately knowing the reaction conditions and controlling them carefully. Therefore, before building a pyrolyzer it is necessary to know what is required of the system and how

the basic reactor parameters affect these requirements.

Some of the basic requirements are:

1. The fragmentation pattern should be characteristic of the parent compound and sufficiently reproducible that a fingerprint file of results obtained from various laboratories could be used for the identification of unknowns. The best characterization is obtained by using a combination of long residence times, and as low a reactor temperature as possible to achieve the desired amount of pyrolysis. The low temperature minimizes the formation of products such as methane, ethylene, propane and propylene which are formed by nearly all organic compounds at high temperatures. These simple products are therefore usually of minimal diagnostic value.
2. The sample should be as small as possible, and yet must be large enough to yield measurable and identifiable peaks upon pyrolysis. If the sample size becomes too large, secondary reactions and recombination products begin to interfere with the examination of the products of the primary fragmentation. The optimum sample size is such that there is no more than one sample molecule per thousand molecules of carrier gas (11) -- this is normally slightly less than one microliter of sample with the usual carrier gas flow rates. To obtain measurable and identifiable

peaks and still be able to inject samples of less than one microliter, it is necessary to use higher reactor temperatures and thus increase the extent of pyrolysis. For PGC to be useful as an analytical method for the effluents of a previous chromatograph, it is desirable that the extent of pyrolysis approach one hundred percent pyrolysis.

3. The reactor should be versatile enough to be used to pyrolyze a wide range of compounds without requiring extensive or time-consuming changes of the equipment.
4. In addition to the above it is desirable that the reactor be inexpensive, relatively simple to construct, and of a design such that it can be easily duplicated in other laboratories.
5. A less important feature at the present time, but one that may become important in the future, is that the automation of the PGC system should be possible without extensive changes.

Because many of these factors are mutually exclusive, some compromises must be adopted. It has been the practice of individuals to adjust the pyrolysis to the optimum for each individual analysis that they run. Since the opinions of various individuals differ as to what constitutes an optimum, this has led to results which cannot be compared except in a qualitative manner.

Up to the present time, the analyses of volatile materials has been carried out using a reactor operated

isothermally. Goforth (14) suggested that there may be some advantage is using a range of temperatures for pyrolysis. A known range of temperatures should be just as definitive and just as reproducible as a single temperature. A reactor incorporating a known range of temperatures would hopefully approach the "ideal reactor" more closely -- a reactor in which every compound is pyrolyzed under optimum conditions. The more easily pyrolyzed compounds would pyrolyze in the part of the reactor maintained at a lower temperature, and the more stable compounds would pass through the lower temperatures and pyrolyze in a region of higher temperatures. Thus all compounds would be pyrolyzed at more nearly their optimum conditions. The assumption inherent in this method is that once a compound is pyrolyzed, further secondary breakdown is minimized.

2. PYROLYZER DESIGN

2.01 GENERAL CONSIDERATIONS

The design of a pyrolysis unit is seemingly a simple mechanical operation. Therefore many people are tempted to just build a reactor, without having any specific design considerations in mind. They then measure the reactor, and calculate the necessary reactor parameters from their finished design. This method often gives a reactor that yields useful results, and therefore improved reactor designs are not sought. To achieve optimum conditions with such a reactor, however, would be a matter of chance. If interlaboratory reproducibility of results is to be obtained the pyrolyzer design must be standardized enough and versatile enough that it can be used with little modification in all laboratories. Because of the versatility that is inherent in the design of a reactor with a temperature range, a reactor of this type should prove to be more useful than a reactor that is operated isothermally.

Pyrolyzer units incorporating a temperature range can be classified into two general types according to the shape of their temperature profile -- stepped temperature reactors and temperature gradient reactors.

Stepped Temperature Reactor

The type of temperature profile in Figure 2.01A has been obtained with filament pyrolyzers by programming the

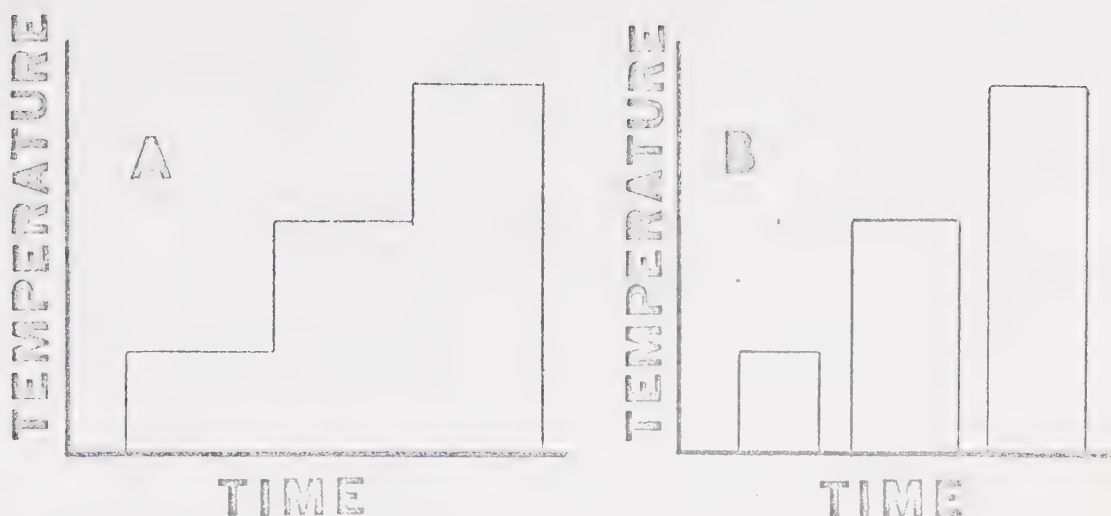


Figure 2.01 Temperature-time profiles of two types of stepped temperature reactors. A. Continuous. B. Broken.

filament voltage in increments at predetermined times.

(23, 31) The normal method of operation is to coat the substance to be analyzed (usually a polymer) onto the filament. The temperature is then raised in steps, and the effluent gases released at each temperature are analyzed by chromatography. Enough substance can be coated onto the filament to span several temperature increments, and the duration, and magnitude of each increment can be easily controlled.

Although the temperature-time profile for a filament operated in this manner is a stepped profile the principle of operation is different from what is desired in a flow reactor. If a flow reactor were operated so that the temperature was increased at set intervals, the effect would be to expose the sample to a temperature range -- not a series of isolated isothermal steps as with the filament reactor.

It would be impossible to distinguish the products formed at one temperature from those formed at any other temperature. In addition, to achieve reproducibility of temperature and residence time, it would be necessary to synchronize the injection of the sample with the programming of the voltage to the heating coil. It would also be necessary to have a method of setting the flow accurately from day to day. The experimental problems involved in doing this are so great that programming the voltage in steps is ruled out as a practical method of achieving the desired temperature profile.

An easier way to obtain the desired temperature profile for the pyrolysis of volatile materials is to connect several isothermal reactors together. This gives a reactor with the desired profile although it may have breaks between the steps. (Figure 2.01B) If several reactors are connected to form a larger reactor the problem of designing a reactor with a temperature range reduces to designing several isothermal reactors and connecting them efficiently.

Residence time calculations are straightforward, and, since the temperature of each step can be specified, comparisons with isothermal data are facilitated because the method of reporting isothermal conditions is in terms of temperature and residence time. It is simple to change the temperature of the steps and thus investigate the effects of various temperature profiles. Also, several of the steps can be operated at the same temperature to give an isothermal

reactor. This makes the comparison of results between stepped temperature operation more convenient and useful, since systematic differences due to differing construction of the reactors are minimized.

An ideal stepped temperature reactor would consist of a large number of steps, each step slightly higher in temperature than the preceding step. This is impractical however, since it would result in a large precolumn dead-space, and make the experimental apparatus extremely complicated. The number of steps must therefore be restricted to a reasonable number (three to six). This means that if it is desired to have a large temperature range within the whole pyrolyzer unit, each step must be considerably higher in temperature than the preceding step. Since the amount of pyrolysis changes strongly with temperature over a narrow temperature range (Figure 2.02) this results in a compound pyrolyzing only a small amount in one step and being extensively pyrolyzed in the next step. Obviously this is little improvement over operation under isothermal conditions.

The above defect can be remedied by decreasing the total temperature range of the pyrolyzer, so that the reactor is composed of several steps differing by small temperature increments. However, the versatility of the reactor is then impaired since only a limited range of samples can be pyrolyzed without changing the whole pyrolyzer temperature range.

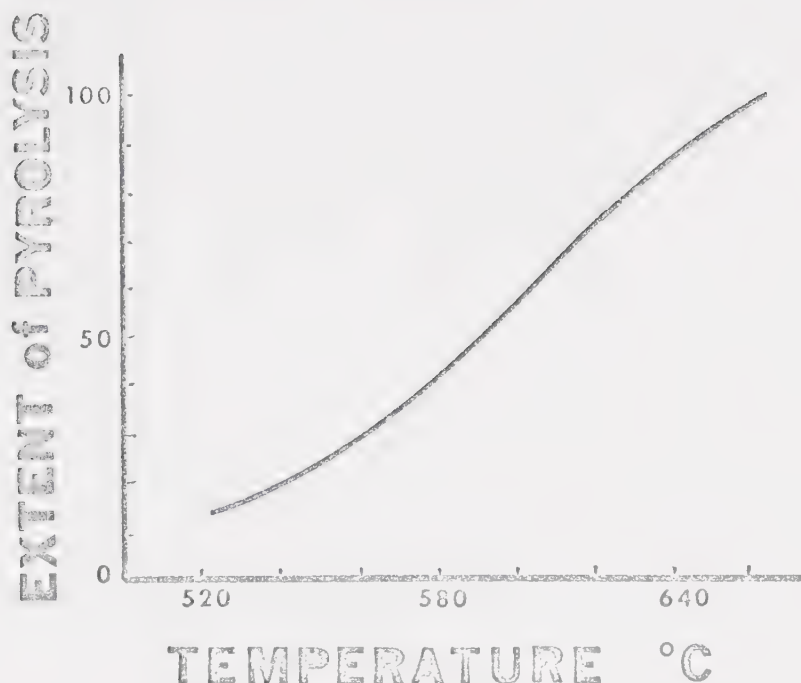


Figure 2.02 Extent of pyrolysis as a function of temperature for 2,3-dimethylbutane in a quartz reactor. Residence time - 6.8 seconds.

Temperature Gradient Reactor

A reactor with a linear temperature gradient was the type of temperature profile originally suggested by Goforth (14). A reactor with this type of profile is similar in concept to the programmed filament of Dal Nogare (6) and can be constructed with either of the profiles indicated in Figure 2.03.

At a first glance these two types of profiles may seem to be equivalent, since time is proportional to distance along the reactor; however, two different types of construction are implied by the figures.



Figure 2.03 Temperature profiles for a gradient reactor.

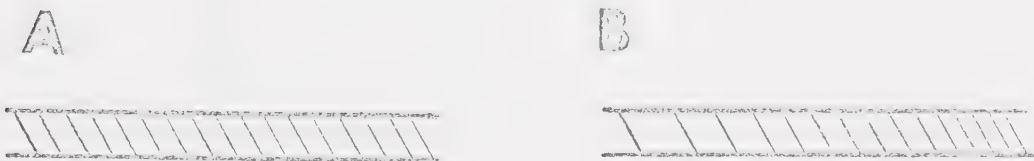


Figure 2.04 Two possible types of coil windings for use in a temperature gradient reactor. A. Uniform coil winding. B. Coil density increasing with distance.

Goforth suggested that a reactor with a profile similar to that in Figure 2.03A could be constructed by winding a tube with a wire such that the coil density increased. (Figure 2.04B) This increase could be in the form of some mathematical function (example: a logarithmic function). The profile exhibited by this winding should then be similar to the shape of the mathematical function to which it is wound.

Another possible method of achieving the gradient

profile is to change the temperature with time (Figure 2.03B) by programming the voltage of a heating coil with uniform coil density (Figure 2.04A). This would result in the temperature of the entire pyrolyzer being increased. The programming is accomplished by using an ordinary wire wound isothermal reactor and switching the power supplied to it (Figure 2.05) from a low voltage to a higher voltage.

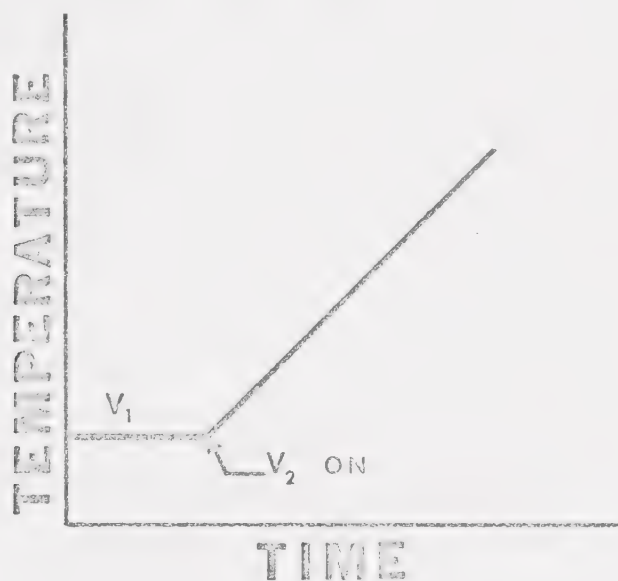


Figure 2.05 Temperature-time profile for a gradient reactor programmed by switching from a low voltage(V_1) to a higher voltage(V_2).

A reactor with a gradient profile has the advantage of being more nearly ideal than a stepped reactor. The gradient reactor has a continuous temperature range which can be specified ($^{\circ}\text{C}/\text{cm}$, $^{\circ}\text{C}/\text{sec}$) and should be able to be duplicated easily. However, to cover a reasonably large temperature range it is necessary either to program at an extremely fast rate (up to $15^{\circ}\text{C}/\text{second}$) or build a long and cumbersome reactor. Programming at a fast rate is difficult

and much of the advantage of this type of reactor is lost, because the conditions change so rapidly that it is impossible for the carrier gas to be in continual thermal equilibrium with the walls of the reactor -- thus the actual reaction conditions are unknown. On the other hand a long reactor is not desirable because it introduces excessive pre-column dead space. It is therefore necessary to adopt some compromise either in the temperature range to be covered, or in the construction of the reactor.

Because the temperature in a gradient reactor is continuously changing the linear flow rate is also continuously changing. Therefore the calculation of the residence time is no longer straightforward. The time spent in the pyrolysis zone can be calculated, but the value calculated cannot be interpreted as a normal residence time since the temperature of the reactor is also changing. Because a single value for the temperature and the residence time cannot be specified it is difficult to make meaningful comparisons with existing isothermal data.

2.02 DESIGN CONSIDERATIONS

Before building a reactor it is necessary to decide what is required of the reactor and how to achieve the desired performance. However, the design is influenced by so many factors that it is inevitable that compromises with ideality must be made to achieve practicality. This

makes standardization of reactor design difficult, but if a reactor is planned carefully these compromises should not have much adverse effect on the reactor performance.

Some of the basic considerations that must be taken into account when designing a pyrolyzer are the material of construction and the physical dimensions of the reactor, the temperature, the temperature profile, and the residence time. These are discussed in more detail in the following pages.

Material of Construction

Various workers have used just about every material (2, 10, 20) that meets the prime requirement of high temperature stability. However, many of these materials exhibit catalytic activity, which tends to obscure the fragmentation due to pyrolysis. Therefore the pyrolyzer should be non-catalytic or only slightly catalytic, which reduces the materials of construction to quartz and gold. Recent studies have indicated that gold is probably the best material for the construction of pyrolyzers (2, 3, 10); however, since it is considerably more expensive than quartz, it would likely only be used when a particular design had been proven. In certain cases gold cannot be used. For instance, if it is desired to build a pyrolyzer that is heated by a coil of resistance wire wrapped around the pyrolyzer tube, it would be necessary to use a non-conducting material such as quartz, or use insulation. However, it is not enough just to insulate the metal tube

because insulation tends to destroy the uniformity of the temperature profile unless it is uniform in thickness.

Physical Dimensions

Because the pyrolyzer in a PGC system is a pre-analytical column attachment it is desirable to have a pyrolyzer with as low a volume as possible since this keeps the pre-column deadspace and the resultant spreading of the sample by longitudinal diffusion to a minimum. The effect of sample spreading is to increase the sample injection time onto the analytical column, which leads to poor column performance. The use of temperature programming with the analytical column enables longer injection times to be tolerated (15), and thus makes it possible to use a pyrolyzer with a significant volume. However, if the precolumn volume is kept to a minimum the system can often be simplified. For instance a shorter length of column may be able to be used or the column may not have to be programmed over a wide temperature range.

The best reactor is a reactor with a large length to diameter ratio (i.e. a long narrow tube) (2, 14, 20). Goforth and Cramers both calculate that the ideal square temperature profile is best approximated by a small diameter tubular reactor. This result is not unexpected since this is the shape which would assure the fastest temperature equilibration with the hot walls of the reactor.

Even though a long, narrow diameter tube is the ideal, it may be advantageous in certain circumstances to sacrifice some of this ideality. A reactor with a large length to diameter ratio also has a large area to volume ratio. The large surface area therefore assures that catalytic or other effects, if significant, will be amplified (2). The result would be a fragmentation pattern that was partly due to catalysis rather than "pure pyrolysis". This makes the pattern difficult to interpret and to reproduce, since impurities could change the catalytic effects greatly. For these reasons it may be desirable to avoid narrow diameter pyrolysis tubes.

The minimum tube radius that can be used may be limited by the availability of various tube sizes for the construction material selected. Similarly the material of construction and space requirements may limit the length of the reactor. It may be necessary to use larger radius tubes than ideal to build the reactor into the most compact space. For example, a wire wound quartz tube cannot be bent without destroying the uniformity of the temperature profile. Therefore, it is desirable to use larger radius tubes than would otherwise be used to fit the reactor into a reasonable space.

Temperature and Temperature Profiles

The ideal temperature profile for an isothermal reactor is a square profile (Figure 2.06). In practice this can only be approximated since it is impossible to change the temperature instantly. The flow rate of the carrier gas, the pyrolyzer dimensions, and the method of heating all influence the squareness of the profile.

According to Levy (20) the flow rate should be low since high flow rates tend to distort the temperature distance profile, (Figure 2.07B) although this effect is minimized by the use of small diameter tubes. The expected variation of the temperature profile with increasing tube radius is shown in Figure 2.07A. The profile is thus supposedly "most square" for a combination of low flow rate and small diameter tubing. However, Goforth (14) has found that the temperature-time profile is best (that is, the ratio of the transition time to the residence time is the lowest) for a combination of high flow rates and long, small diameter reactors. He also warns against using only the length of the transition zone to determine the optimum flow rate, since the wrong conclusion (low flow rates are best) would be drawn.

The time that the gas takes to come to thermal equilibrium with the walls of the reactor can be calculated by the method of Giddings (13) and Rummens (25) using the Einstein diffusion equation. Using their method it is

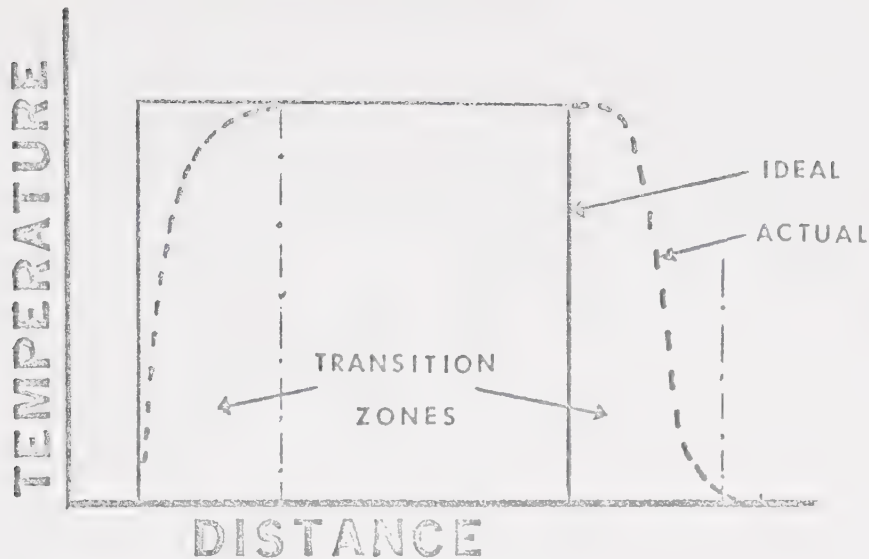


Figure 2.06 Idealized temperature profile for an isothermal pyrolyzer showing how the actual profile differs from the ideal profile.

possible to calculate a tube diameter which will assure that the time taken for heat transfer is small compared with the residence time. It is then necessary to design a reactor so that the transition zones are also small compared to the residence time. This can be done by making the constant temperature zone large compared to the transition zones; using a heating method that has a sharp temperature front; or a combination of both methods. However, it must be recognized that some compromise will probably be necessary since the length of the constant temperature zone cannot be increased without affecting the other reactor parameters.

The method used to heat the reactor can also influence the temperature profile. If the pyrolyzer is immersed in a furnace or heated by some other method which gives a sharp temperature front, the temperature profile will approach

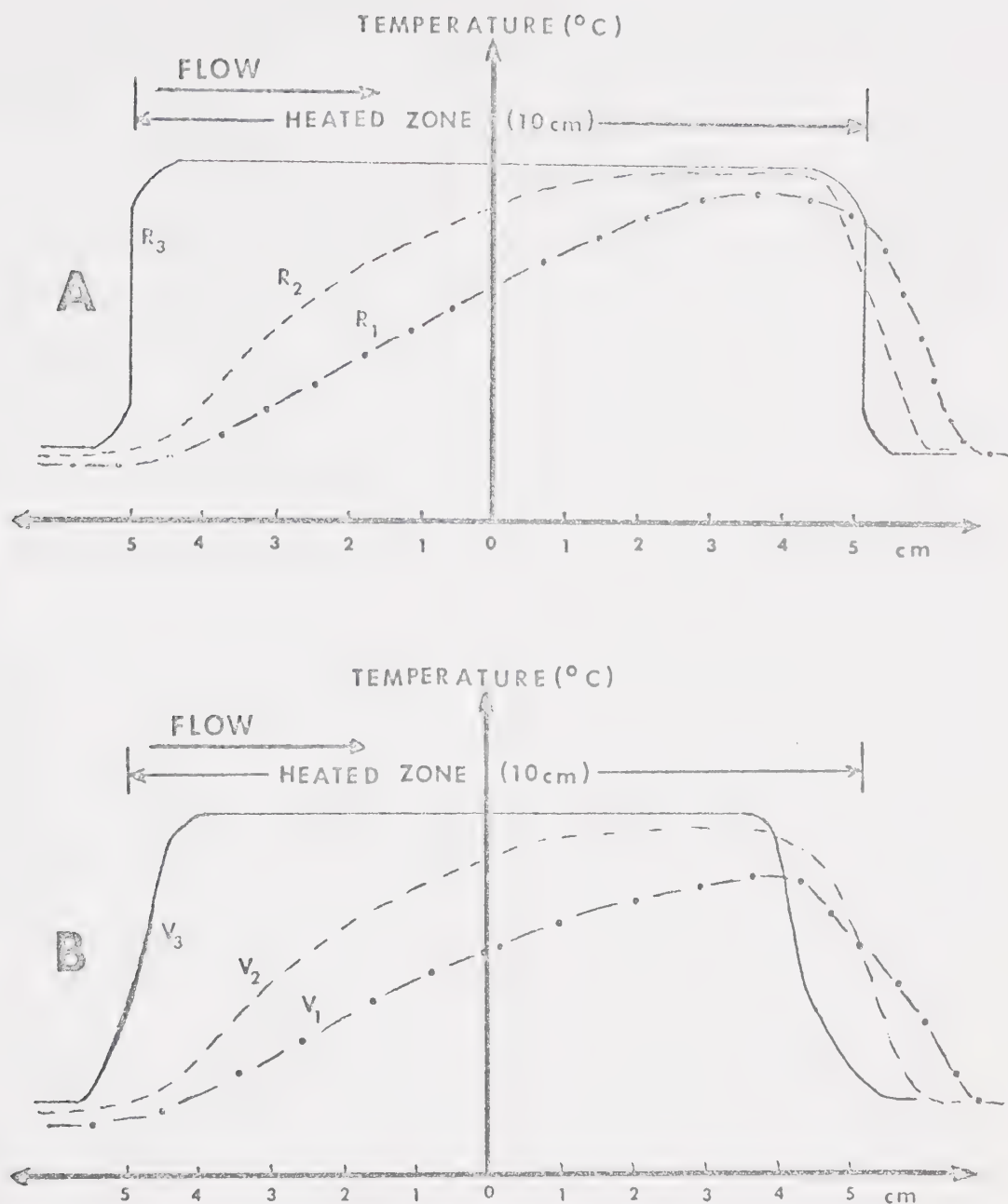


Figure 2.07 Schematic presentation of expected temperature profiles along the axis of externally heated cylindrical microreactors. A. Expected profiles of microreactors of different internal diameters ($R_1 > R_2 > R_3$) and same linear velocity of carrier gas. B. Expected profiles of a microreactor operated at different linear velocities of the carrier gas ($V_1 > V_2 > V_3$) assuming non-turbulent flow. (copied from Levy (20))

squareness. For the temperature front to be sharp no heating should take place prior to the entrance of the pyrolyzer. At the entrance of the pyrolyzer the temperature should be the desired pyrolysis temperature. If, on the other hand, a wire wound reactor is used the transition zones are broadened, because the reactor temperature does not increase as sharply as it does in a furnace reactor. The reason for this is that the ends of the wire coil tend to get stretched slightly more than the middle of the coil does, thus the coil density at the ends is less and the temperature is lower.

The temperature at which the pyrolysis unit is operated is dependent on the sample to be pyrolyzed. As was stated before there is no ideal temperature -- the optimum conditions are a compromise between temperature and residence time. For example, 85% pyrolysis can be obtained from 2,3-dimethylbutane under either of the following sets of conditions with almost identical product distribution.

Residence time = 27 sec
Temperature = 575°C
Amount of pyrolysis 86%

Residence time = 7 sec
Temperature = 645°C
Amount of pyrolysis 89%

However, if the temperature were increased much more, products such as methane and ethylene would start to predominate more strongly relative to the other products. Correspondingly, to achieve the same amount of pyrolysis using a lower temperature it would be necessary to use very long residence times.

Regardless of what temperature is used it is essential

that the temperature be accurately known, easily monitored and reproducible. This is easily accomplished in a good furnace reactor but can present difficulties in a wire wound reactor.

Residence Time

The other important reaction variable which must be accurately known and controlled is the residence time. Sutton and Harris (28) found that long residence times (6 to 25 sec) give the best results; however much of the data in the literature has been obtained using short residence times (less than two seconds).

To control the residence time accurately it is necessary to control the flow rate accurately. Long residence times require either low flow rates or long pyrolysis tubes. However, Goforth (14) calculated that a high flow rate gives the most desirable ratio of the transition time to the residence time. Since a low flow rate is often not compatible with the optimum operation of the gas chromatograph in a PGC system, and long pyrolysis tubes are cumbersome, it is normally necessary to sacrifice the performance of either the gas chromatograph or the pyrolyzer unit. Since most of the data in the literature has been obtained at small residence times it is apparent that most workers, up to now, have elected to sacrifice the performance of the pyrolyzer.

However, using a system similar to that used by

Goforth (14) it is possible to control the flow through the pyrolyzer and the analytical column separately. Thus, both may be operated under optimum conditions. With the flow through the pyrolyzer known, and controlled, it is possible to calculate without difficulty the time spent in the pyrolysis zone.

2.03 PRELIMINARY REACTOR DESIGN

From the discussion in the previous section it would seem that a quartz tube heated by a coil of resistance wire would be an undesirable type of reactor. However, a reactor of this type has many advantages for use in a pyrolyzer incorporating a temperature range. First, quartz tubing is stable at high temperatures and possesses little catalytic activity. It is also readily available in various sizes. Since a stepped temperature reactor requires several connected isothermal stages, it is more convenient, cheaper and more conserving of space to use several wire wound reactors than to use several furnaces. A wire wound reactor also has the advantage that it is relatively easy to construct and is therefore easily replaced if broken. This type of reactor can also be easily converted to operation as a temperature gradient reactor by programming the heating coil. This facilitates comparison between stepped temperature operation and temperature gradient operation. Thus a wire wound reactor is an easily constructed, versatile reactor. It

was therefore decided to use this type of reactor in spite of the difficulties associated with it.

Several preliminary reactors were built to determine the temperature profiles that could be obtained from various coil windings. At first, an attempt was made to wind the coil by hand, trying to space the coils evenly. This resulted in a reactor with a wildly varying temperature profile (Figure 2.08). Insulating the reactor made little difference -- the temperature was increased but there was little improvement in the temperature profile. The conclusion reached from this was that the winding must be uniform -- that is, the coil density (the number of coils per unit length) must be constant if a uniform profile is to be achieved. This was accomplished by using the following procedure for winding. A mandrel of the same size as the pyrolyzer tube was selected and the resistance wire was then wound as closely as possible (adjacent coils touching) around this mandrel. A length one-third to one-half of the desired coil length was wound and then the coil was stretched to the desired length. The ends of the coil where the stretching was not uniform were cut off. The remaining coil was then removed and placed on the pyrolysis tube. When the coil was freshly wound there was considerable "springiness" and the coil had to be securely fastened. However, after the coil had been strongly heated several times this springiness disappeared. This method gave windings with a uniform coil density and thus resulted in a reactor with a

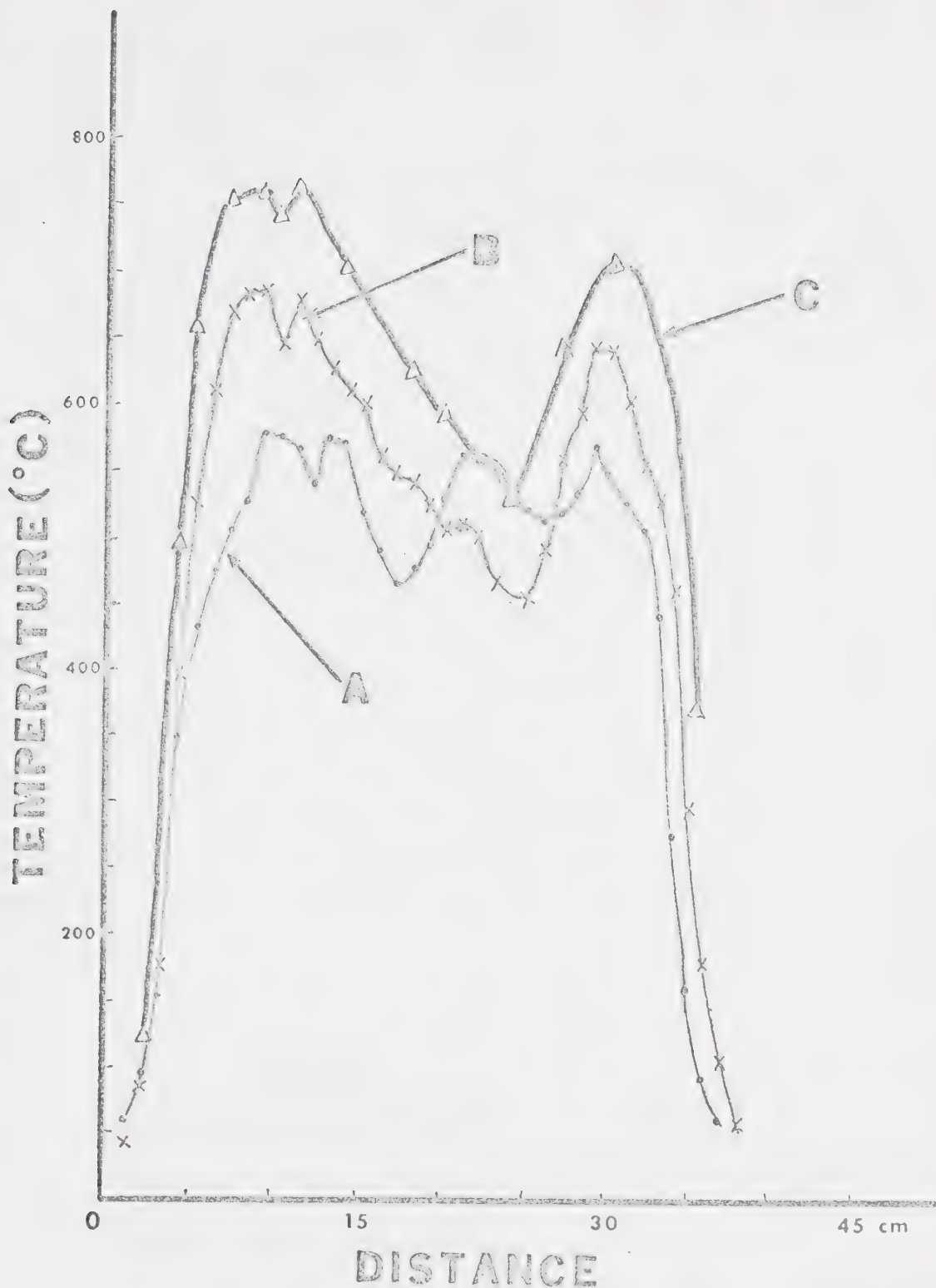


Figure 2.08 Temperature profiles of hand wound reactors. A. Reactor wrapped with asbestos tape, then coil wound onto the asbestos tape, then another layer of asbestos tape added. B. Coil wound directly around tube and then insulated with asbestos (two layers). C. Same as B except that a glass jacket was placed around the pyrolyzer in addition to the asbestos insulation.

much more uniform temperature profile (Figure 2.09B).

It was thought that if a coil could be wound and stretched so that there were windings of two different coil densities the resultant temperature profile would be stepped. To obtain this type of winding one-half of a closely wound coil was stretched a certain amount and the other half a differing amount (Figure 2.10). This did yield a stepped profile, (Figure 2.09A) however there was some temperature fluctuation near the junction of the windings. This is probably due to the uneven coil density in this region since non-uniform stretching results from having to hold this part while either end is stretched. A reactor with three steps was constructed in a similar manner. The profile of this reactor can be seen in Figure 2.09C. A stepped temperature profile can be achieved by this method of winding; however, a reactor of this type has several disadvantages.

1. The temperature of the individual steps can not be changed by changing the power applied without changing the temperature of all the steps. Therefore, the temperature of each step is not independently controllable.
2. The total temperature range that can be covered is limited since a long reactor is necessary and such a reactor is inconvenient, and increases the difficulty of construction.



Figure 2.09 Temperature profiles of some preliminary stepped reactors. A. Two stage reactor. B. Isothermal reactor. C. Three stage reactor.

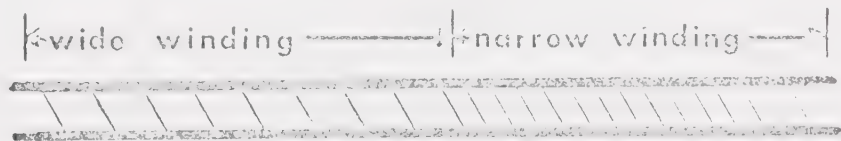


Figure 2.10 Example of a wire wound reactor composed of windings of two different coil densities.

3. There is no way of predetermining the temperature of each step. The reactor must be built and the temperature of each step measured. This means that it would be difficult to duplicate a reactor.

For the above reasons it was decided that a reactor consisting of isolated windings would be preferable since then the temperature of each step could be controlled independently, and be continuously variable.

A reactor of several steps could be built in several configurations. It could consist of one long reactor with several windings or several shorter separate reactors (see Figure 2.11). A configuration such as 2.11A creates several problems. First, it is clumsy, and takes up a large linear space. Measuring the temperature is difficult since a long thermocouple is required. Also the length

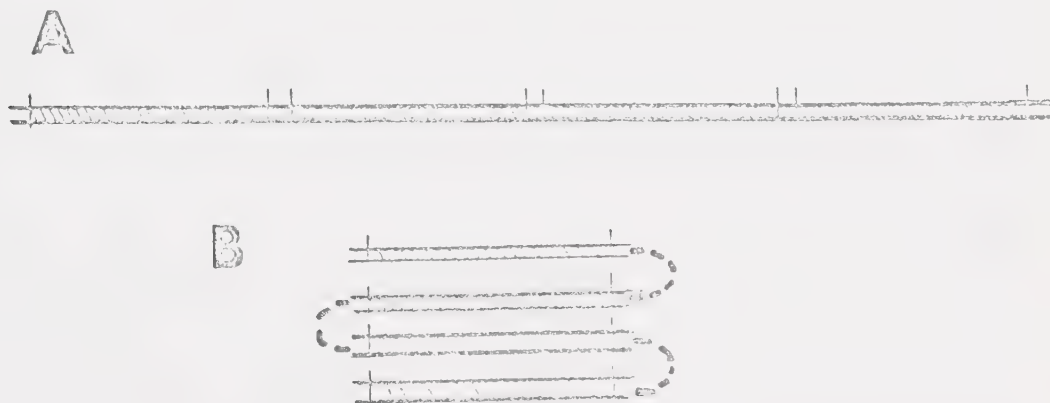


Figure 2.11 Two possible configurations for a stepped reactor consisting of several stages. A. Continuous reactor. B. Separate reactors.

A configuration such as 2.11B requires extra volume for connections but it has the advantages that the temperature can be measured more easily, the reactor can be built into a compact volume, and injections can be made into any one of the pyrolysis tubes.

2.04 STEPPED TEMPERATURE REACTOR

It can be seen from the preceding discussion that useful reactor design is a compromise between what is ideal and what is practical. When designing a reactor one is faced with a multitude of interconnected parameters -- changing one parameter results in changes in the other parameters. The design problems are considerably reduced if certain arbitrary decisions are made with respect to certain parameters and the other parameters adjusted accordingly.

The first design decision that must be made for a stepped temperature reactor is the number of steps in the reactor. Ideally, the number of steps should be as large as possible, but for practical reasons the number of steps must be kept reasonable.

It was arbitrarily decided to build the reactor with four isothermal steps. This number is small enough that the total reactor size can be kept reasonably small and the heating apparatus uncomplicated. Four steps should also be enough to determine whether or not a stepped temperature

reactor is useful. Four reactors also allow a reasonable range of temperature across the whole unit and provide enough stages so the profile can be varied sufficiently to determine some effects of changing the temperature profile.

Another parameter that can be arbitrarily fixed to facilitate design is the residence time. It has been found that the amount of pyrolysis and the fragmentation changes relatively little between six and twenty-five seconds residence time (17, 28) but changes sharply below about six seconds. Thus it is an advantage to use a reactor such that the residence time is in the range of six to twenty-five seconds since minor variations in residence time would not result in large variations in results.

It was therefore decided to build the reactor so that each step had a residence time of five to seven seconds and the total residence time was about twenty-five seconds. The residence time can be calculated from the formula

$$\tau = \frac{V_p}{F_p} \quad (2-1)$$

where τ is the residence time, V_p is the volume of the reactor, and F_p is the volumetric flow rate through the pyrolyzer.

A desired residence time could theoretically be obtained by using any one of many possible volume to flow rate ratios. However, other considerations limit the choice of flow rate considerably. To reduce the deadspace the volume of the reactor should be kept as small as possible.

Therefore, it becomes necessary to use low flow rates to obtain the desired residence time. It must be realized, though, that the use of low flow rates increases the ratio of the transition time to the residence time (14). Some compromise must therefore be made between the volume and the flow rate to obtain the best conditions and the most convenient construction for the pyrolysis tube.

To facilitate connecting the reactor to the other equipment in the system, and to conserve space, it is desirable to be able to fit the reactor into as small a space as possible. This is also desirable because it is difficult to prepare a long heating coil that is uniform over its whole length. It was therefore arbitrarily decided to use 3.8mm inner diameter tubing (6mm o.d.). This was chosen because Swagelok quarter inch fittings can be used as connectors and the desired residence times can be obtained using reasonable lengths of tubing.

Since the temperature in each step is increasing the volumetric flow rate in the pyrolyzer tube is also increasing. The flow in the pyrolysis tube can be calculated from the flow at room temperature from the equation;

$$F_p = F_o \frac{T_p}{T_o} \quad (2-2)$$

where F_o is the flow at the entrance to the pyrolysis unit, T_p is the temperature of the pyrolysis tube and T_o is the temperature at which the flow is measured.

This means that if the same residence time in all tubes is desired, the length of the tubes must be increased with increasing temperature. The residence time can thus be calculated as

$$\tau = \frac{\pi r^2 L T_o}{F_o T_p} \quad (2-3)$$

where L is the length of the reactor, r is the radius of the quartz tubing. Rearranging Equation (2-3) the length of tubing required for a given residence time can be calculated.

$$L = \frac{\tau F_o T_p}{\pi r^2 T_o} \quad (2-4)$$

This length would be the length of the constant temperature zone. An additional length on each end of this zone is required for the transition zone -- to allow the temperature to reach the desired level. It was determined from preliminary designs that, at the flow rates used, the temperature reaches a nearly constant value within three centimeters after heating is started. Therefore, an additional six centimeters would have to be added onto the length of each reaction zone calculated from Equation 2-4

Four pyrolysis tubes were built to the dimensions in Table 1. These dimensions were calculated for the temperatures given and a residence time of six seconds. To simplify the design further it was decided to use a flow through the unheated system (F_o) of approximately ten milliliters per minute. The tubes designed to the

specifications in Table 1 were used for all later work even though the temperatures of the stages were changed considerably. (see appendix for details)

Each tube was constructed as indicated in Figure 2.12. It was found to be extremely difficult to connect the pyrolysis tubes since the connection was so close to the hot zone of the tubes. The method that was found best was

TABLE 1 DESIGN SPECIFICATIONS FOR PYROLYSIS TUBES FOR A STEPPED TEMPERATURE REACTOR

Pyrolyzer tube	Heating element	Length of constant temperature zone	Length of heated zone	Temperature °C
P ₁	#26 Nichrome wire(35 ohms)	20 cm	26 cm	410°
P ₂	#24 Nichrome wire(25 ohms)	22 cm	28 cm	490
P ₃	#24 Nichrome wire(31 ohms)	24 cm	30 cm	560
P ₄	#24 Nichrome wire(32 ohms)	26 cm	32 cm	630

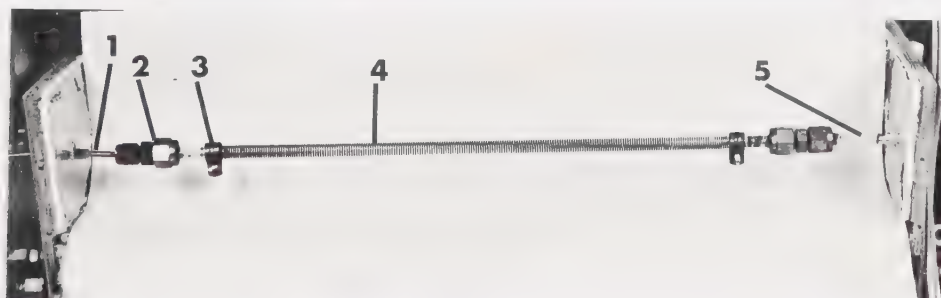


Figure 2.12 Details of the construction of the pyrolysis tubes. 1. One-eighth inch copper tubing. 2. Swagelok connector. 3. Rubber tubing clamp(electrical contact). 4. Coil. 5. 6 mm o.d. tubing.

to make a ferrule of teflon tape by wrapping thin strips of tape around the quartz tube and then compressing this into the swagelok connector. This resulted in a gas-tight seal, that could be tightened without fear of cracking the quartz tube.

Because of the springiness of the coil, the following method was used to fasten the coil to the tube and to make electrical contact. A piece of one-quarter inch copper tubing about one-half a centimeter long was cut and split. This was then wrapped around the coil and a three-eighths inch rubber tubing clamp placed over it. By screwing the clamp tight the copper tubing was compressed and the coil could be held in place (Figure 2.13). After heating, the

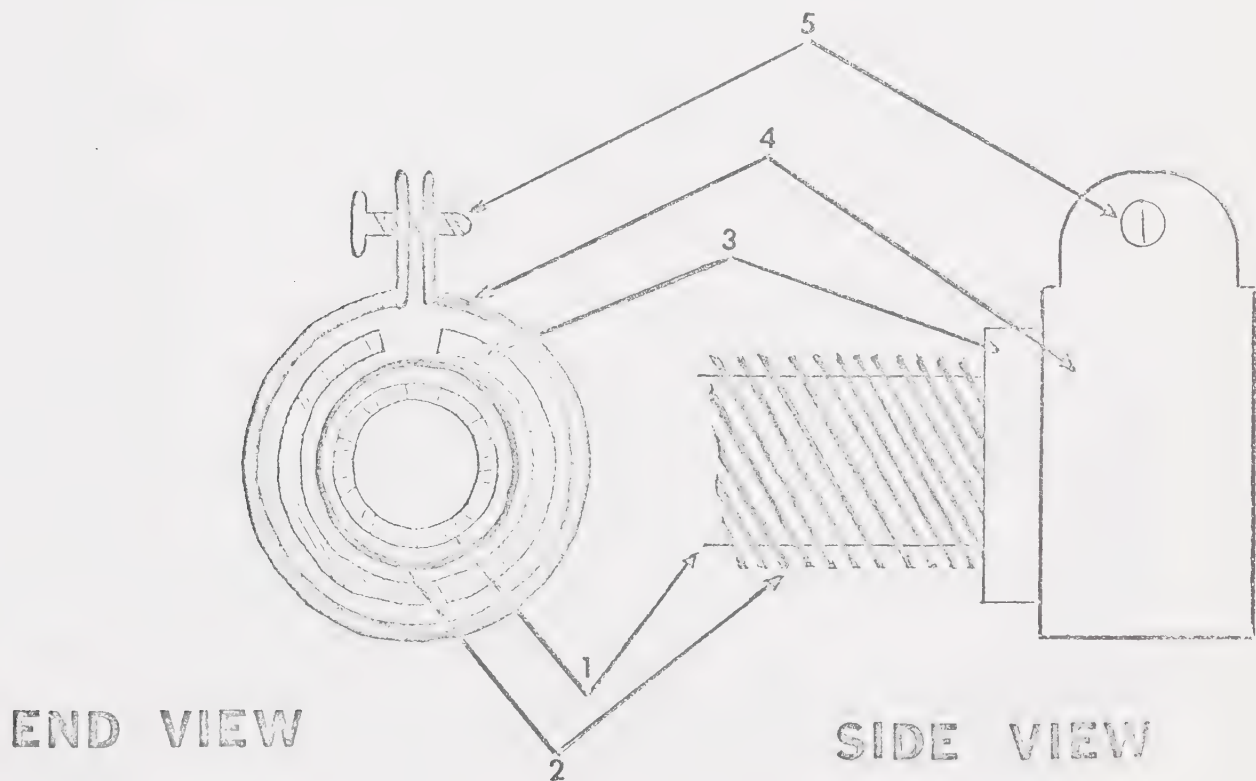


Figure 2.13 Method of holding coil in place and making electrical contact. 1.. Quartz tubing. 2. Coil. 3. Piece of split copper tubing. 4. Rubber tubing clamp (3/8 inch) 5. Screw to tighten clamp and to which electrical contact was made.

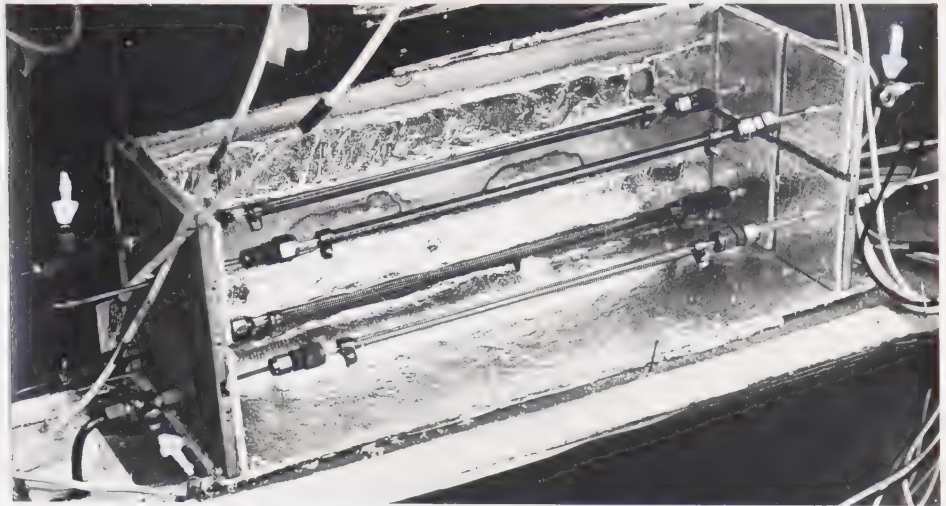
coil was not springy, however, the clamp still had to be tight to hold the coil from slipping when it was heated. Electrical contact was made by fastening small alligator clips onto the screw of the clamp.

The four tubes were mounted in a box of one-eighth inch asbestos coated with aluminum foil. The tubes were positioned in the manner indicated (Figure 2.14 A and B). Each tube was isolated in a separate compartment by dividers of asbestos coated on both sides with aluminum foil. This was done in an attempt to keep the calibration of the temperature independent of the temperature of the other tubes and was reasonably successful. For example, if tube two were being calibrated, the temperature was only about five degrees warmer when the other tubes were hot, even though the temperature in the other compartments was about 150° C.

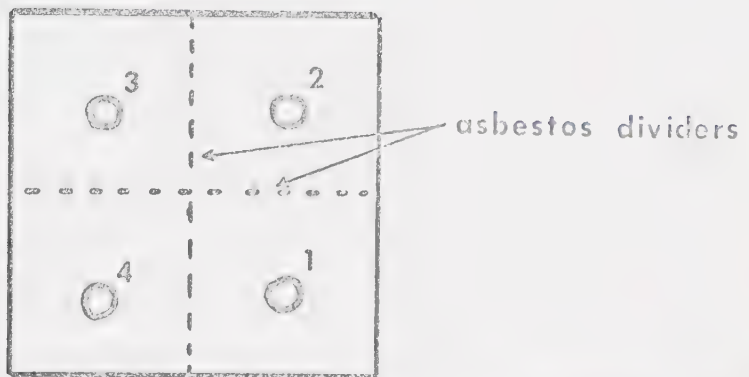
Injection ports (Swagelok Tees) were placed at the entrance of each pyrolysis tube. Because of the construction of the box containing the pyrolysis tubes, it was not possible to place the injection ports inside the box. The injection ports were therefore placed immediately outside the box and were heated by heating tape.

The box was completely enclosed by asbestos shielding (Figure 2.14C). This protected the tube from drafts. Because of this it was found that the tubes did not have to be insulated individually -- the wire was wrapped around the tubing directly and then the tube was placed in the box.

A



B



C



Figure 2.14 The pyrolysis box showing positions of the pyrolysis tubes and the construction of the box. (A,B) Arrangement of the pyrolysis tubes- note position of the asbestos dividers. C. Outside appearance of the box- the injection ports are marked with an arrow.

This facilitated replacement of the tubes when they were broken because the coil could be removed easily and used again on another piece of tubing.

The asbestos box was built so that the longest tube would just fit inside. Because of the differences in the lengths of the tubes, this meant that the shorter tubes had to be supported, and longer connections were used. The connections at one end of the box were made of one-eighth inch copper tubing and swagelok connectors. However, since it was necessary to measure the temperature profile of the tubes, larger tubing was used at the other end of the box so that a thermocouple could be passed into the tube. The glass tubing adds considerably to the volume; however it was unavoidable since the thermocouple would not pass through smaller tubing. This arrangement had one advantage. When a tube was being removed the connectors could be loosened and the glass tubing pulled to the right (Figure 2.12). This made the removal of the tube easy. Similarly, when replacing the tube, the tube could be positioned and the glass tubing pushed in so that the connectors met. This avoided placing undue strain on the pyrolysis tube.

As explained in earlier sections the ideal temperature profile for a pyrolyzer is a square profile. It is difficult to approximate this profile with a wire wound reactor because of the relatively long transition zones inherent in the design of such a reactor.

The uniformity of the profile is dependent on the

uniformity of the coil density -- even small variations in coil density result in large temperature fluctuation (Figure 2.08). Because of this, construction of a heating coil is largely a matter of trial and error. Often several attempts were required before a coil with the desired characteristics was obtained. Another source of temperature fluctuations was found to be the quartz tubing itself. Small variations in diameter or wall thickness and small faults led to fluctuations which were not due to coil design. It was therefore necessary to test every coil on several tubes to determine if the profile was reproducible.

The temperature was read by pushing a thermocouple into the tube and removing it a centimeter at a time. The temperature was read on an API pyrometer with a 0 to 1100°C scale. After each movement of the thermocouple about three minutes was allowed for the thermocouple to come to equilibrium. The thermocouple could not be placed in the pyrolysis tube under actual operating conditions because of the possible catalytic effects that could result. This meant that the temperature of the pyrolysis tube was not monitored under operating conditions. Therefore a calibration of temperature versus amperage was made and the temperature under operating conditions adjusted by adjusting the amperage. However, it was found that the temperature drifted considerably with time from the calibrated value. This was probably due to the changes in the resistance of the coil. To try to overcome this defect the temperature was calibrated against wattage applied. This too, drifted

slowly, but over a much longer period and not as much. This drift in temperature calibration is the most likely source of error in the temperature readings. For this reason, frequent recalibrations were needed to insure that the temperature was what it was presumed to be. There are several other possible sources of error in the temperature readings. One is the variations in the coil itself. Another possible source of error is the position of the temperature sensing portion of the thermocouple. It was found that the temperature could vary as much as fifteen degrees when the thermocouple was rotated without changing its longitudinal position. Because it is extremely difficult to wind a uniform coil it was considered that any profile where seventy percent of the readings were within seven degrees of the median temperature was sufficiently uniform (see appendix for details). The cumulative effect of all the uncertainties is that the temperatures quoted in this thesis probably have an uncertainty of about ten degrees centigrade (i.e. a temperature quoted as 600°C is actually $600^{\circ}\text{C} \pm 10^{\circ}\text{C}$).

The measurements of the temperature profile were taken without flow through the pyrolysis tubes. When the measurements were taken with flow, the effects indicated in Figure 2.15 were observed as expected. Although some change would also have been expected at the beginning of the profile, none was observed. The difference from ideality at the end of the profile is probably due to conduction along the tube and heat transfer by the hot gases.

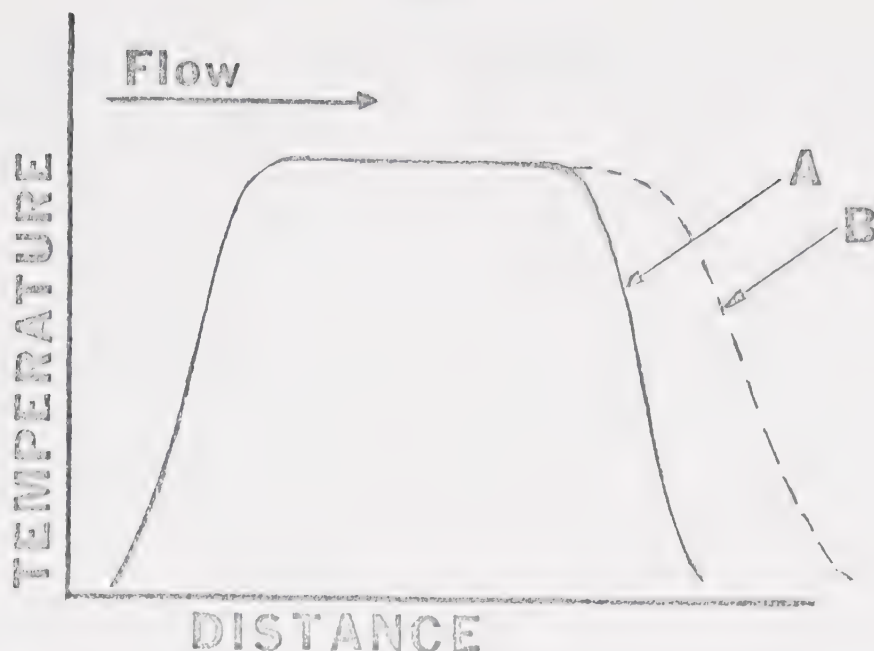


Figure 2.15 Effect of the flowing carrier gas on the temperature profile. A. Temperature profile measured without gas flow. B. Temperature profile measured with gas flow.

Calculations involved with Stepped Temperature Reactors

The time a molecule takes to come to thermal equilibrium with the walls of the pyrolysis tube is approximately equal to the time required for a molecule to travel a distance of one-half of tube diameter (25). The time can be calculated from the Einstein diffusion equation by the method given by Giddings (13).

$$\sigma^2 = 2 D t_D \quad (2-5)$$

where σ is the displacement, t_D is the time over which the diffusion occurs and D is the diffusion coefficient. This

equation can then be used to estimate the time required for the desired displacement

$$t_D = \frac{d^2}{2 D} \quad (2-6)$$

where d is the displacement. Thus, if d is one-half of the tube diameter and the tube diameter is 0.38 centimeters, Equation 2-6 becomes

$$t = \frac{0.018}{D} \quad (2-7)$$

The diffusion coefficient can be calculated by the method of Chen and Othmer (5) (see appendix for details). The diffusion coefficient will be at its lowest value at the entrance of the pyrolyzer since the temperature is the lowest at the entrance also. The time taken for equilibration will thus be the longest during the transition zone.

Rummens (25) calculated the time for thermal equilibration using the diffusion coefficient of the sample molecule. A time calculated by this method should be regarded as a maximum time since the ratio of the helium molecules to sample molecules in the pyrolysis tube is approximately one thousand to one. Therefore most of the heat exchange will be due to diffusion of the helium molecules to the walls of the pyrolysis tube. The diffusion coefficient of helium in helium is considerably greater than the diffusion coefficient of normal hexane (a typical sample molecule) in helium; therefore the time required for thermal equilibration

as calculated from Equation 2-7, using the diffusion coefficient of helium in helium, would be significantly less than the time calculated using the diffusion coefficient of the sample molecule (see Table 2). As the temperature rises the time taken for thermal equilibration becomes less because the diffusion coefficient becomes larger.

TABLE 2 CALCULATED TIMES FOR THERMAL EQUILIBRATION WITH DIFFERENT DIFFUSION COEFFICIENTS*

298°K 1 atm $^{\text{D}}\text{He-He}$	t	298°K 1 atm $^{\text{D}}\text{He-n-hexane}$	t
$1.95 \text{ cm}^2\text{sec}^{-1}$	0.019 sec	$0.313 \text{ cm}^2\text{sec}^{-1}$	0.12 sec
* see Appendix for details of calculations			

To calculate the residence time from Equation 2-3, the flow through the pyrolyzer must be known. Figure 2.16 shows a diagram of the flow system used. This method of adding flows to optimize flow through the pyrolyzer and the column is similar to that used by Goforth (14). The flow was measured at the outlet of the system and corrected to 273°K and one atmosphere pressure, by the following equation.

$$F_m^O = F_m \frac{(P - P_w) 273}{760 T} \quad (2-8)$$

where F_m^O is the measured flow corrected to standard conditions, P is the atmospheric pressure in mm of mercury P_w is the vapor pressure of water in mm of mercury, and T

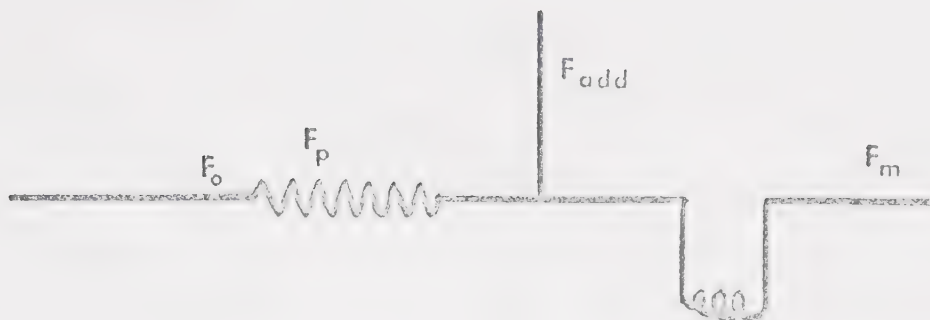


Figure 2.16 Diagram of the additive flow system used. F_o is the flow at the entrance to the pyrolyzer tube, F_p is the flow within the pyrolyzer, and F_m is the flow measured at the outlet of the system.

is the temperature ($^{\circ}\text{K}$) at which the flow is measured.

The flow at the entrance to the pyrolyzer tube (F_o) can then be written as

$$F_o = F_m^o \frac{p}{p_{py}} \quad (2-9)$$

where p_{py} is the pressure within the pyrolysis tube. As F_{add} (Figure 2.16) is increased the pressure in the pyrolyzer increases by p_{add} . The flow at the entrance to the pyrolyzer then becomes

$$F_o = F_m^o \frac{p}{p_{py} + p_{add}} \quad (2-10)$$

To calculate the residence time the corrected flow (F_o) from Equation 2-10 is substituted in Equation 2-3 to yield

$$\tau = \frac{r^2 L T_o (p_{py} + p_{add})}{F_m^o T_p p} \quad (2-11)$$

Details of the calculations and the calibration charts can be found in the appendix.

2.05 TEMPERATURE GRADIENT REACTOR

Theoretically a temperature gradient reactor could be built using either of the heating methods described in Figures 2.03 and 2.04. The original suggestion of Goforth (14) was to use a tube wound with increasing coil density. However, since it was found to be difficult to wind a uniform heating coil for isothermal use by hand; it was thought that it would be almost impossible to obtain a coil with a regularly increasing temperature profile by hand winding. This means that it would be necessary to wind the coil using a lathe or some other similar device.

Since the coil must be wound to a predetermined mathematical pattern, it would be difficult to wind, even on a lathe. Once the coil was wound it would also have to be handled carefully since slight changes that occurred in fastening the coil to the pyrolysis tube (i.e. stretching part of the coil) could destroy the uniformity of the temperature profile. Because of the difficulties associated with the winding, the coil would also be difficult to replace, or duplicate. Another disadvantage of this type of coil winding is that the temperature gradient would not be widely variable, since the gradient is controlled by the mathematical pattern to which the coil is wound, and could be changed only slightly by varying the power applied to the coil.

The method of programming the heating coil voltage is much more convenient and versatile. It is possible to use

an isothermal wire wound reactor, which simplifies the design of the heating coil since the coil can be wound without undue difficulty (see section 2.03). The voltage to the coil can be programmed simply -- all that is necessary is to switch from a low voltage power source to a higher voltage source (Figure 2.17). Using this type of system it is possible to vary the heating rates considerably. The gradients obtained are approximately linear over short time ranges. (Figure 2.18) (See appendix for other details).

Because it is so easy to convert a stepped temperature reactor to a programmed voltage temperature gradient reactor, it was decided to make the gradient reactor of this type. Pyrolyzer tube P_4 (See Table 1, Section 2.04) was

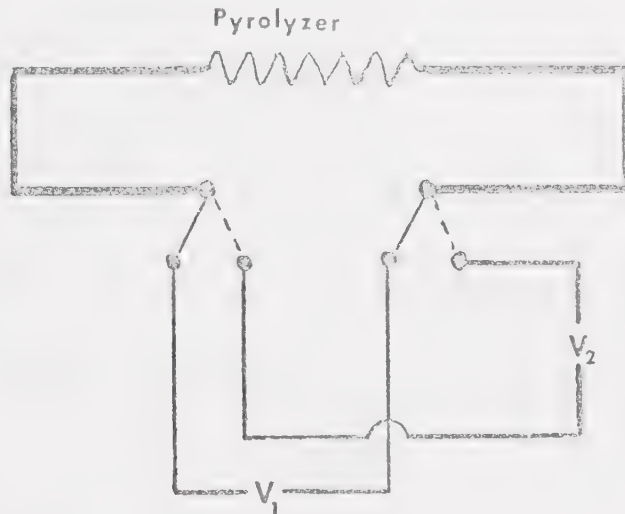


Figure 2.17 Programming system for the temperature gradient reactor. The programming is accomplished by switching from a low voltage power source (V_1) to a higher voltage power source (V_2).

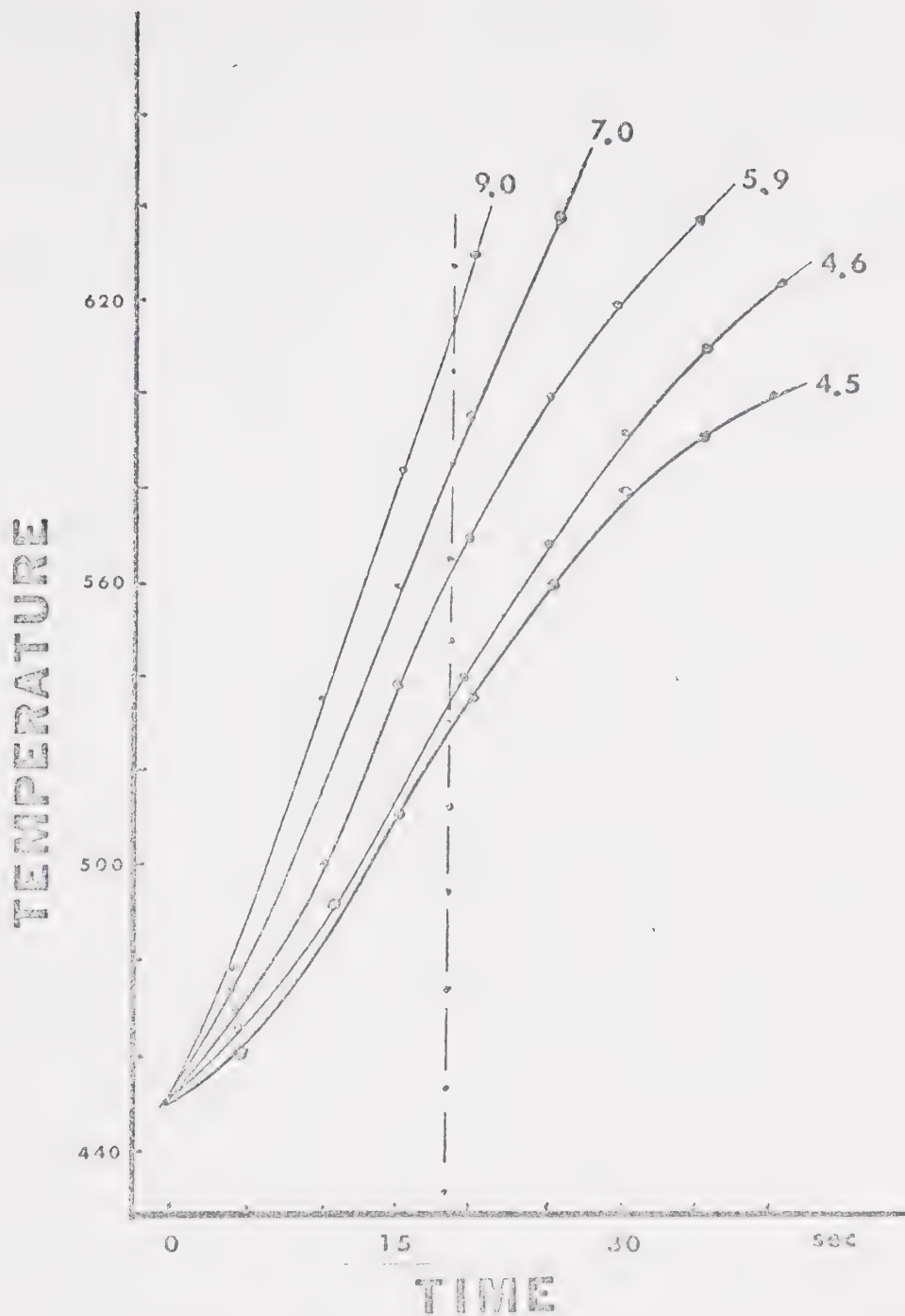


Figure 2.18 Temperature gradients obtained with the gradient reactor starting at an initial temperature of 450°C. Numbers on the graph are the heating rates in degrees Centigrade per second.

converted to programmed operation using a d.p.d.t. switch to switch between two variacs in an experimental set-up similar to that illustrated in Figure 2.17.

The temperature gradient was measured by placing a thermocouple about midway through the pyrolyzer, adjusting the temperature of the pyrolyzer to the desired initial temperature, and then switching to a higher voltage. The temperature was monitored on a recorder fitted with a device for bucking the voltage from the thermocouple so that the recorder pen could be set to zero, regardless of the initial temperature of the pyrolyzer. This procedure enabled the temperature change to be recorded and the voltage due to the initial temperature cancelled. Figure 2.18 shows some typical gradients that were obtained. As can be seen the temperature tends to reach a maximum rate of increase. This is due in part to the fact that the thermocouple has a finite heat capacity and cannot respond to a temperature change instantly. The temperature read from the thermocouple therefore lags behind the actual temperature. At high programming rates the recorded temperature will thus be continually lagging the actual temperature. The faster the programming rate the more the thermocouple will lag until a point is reached where the programming rate is faster than the response time of the thermocouple. At this point the recorded temperature will be only an indication of the response of the thermocouple since the temperature will be increasing faster than the thermocouple. The maximum programming rate shown in Figure 2.18 is close

to the response speed of the thermocouple. This was determined by heating the pyrolysis tube, and then shoving the thermocouple into the tube and noting the time required for the thermocouple to reach a steady reading. Errors in temperature caused by the finite response time could be minimized by using thermocouples of low heat capacity.

Because the temperature of the reactor is continuously increasing, the volumetric flow rate is also increasing. The flow through any portion of the tube can be written as

$$F_1 dt = dV$$

where F_1 is the instantaneous flow rate, dt is a time increment and dV is a volume increment. Since

$$F_1 = F_0 \frac{T_1}{T_0}$$

where T_0 is the temperature ($^{\circ}\text{K}$) at the entrance to the pyrolysis tube and T_1 is the instantaneous temperature ($^{\circ}\text{K}$), the above equation can be written as

$$\int_{t=0}^{t_p} F_0 \frac{T_1}{T_0} dt = \int_{V=0}^{V_p} dV \quad (2-12)$$

where t_p is the pyrolysis time and V_p is the volume of the heated zone of the pyrolyzer. The temperature increase in Figure 2.18 is approximately linear in the desired time range (0 to 20 seconds), therefore, the instantaneous

temperature is

$$T_i = T_o + Rt$$

where R is the programming rate. Substituting this expression for T_i in Equation 2-12 and integrating over the specified limits, Equation 2-12 becomes

$$\frac{F_o}{T_o} \left[T_o t_p + \frac{R t_p^2}{2} \right] = V_p$$

This equation can be arranged to yield expressions for the required initial flow rate for a specified pyrolysis time (Equation 2-13) or the pyrolysis time itself (Equation 2-14)

$$F_o = \frac{2 V_p}{\left[2 t_p + \frac{R t_p^2}{T_o} \right]} \quad (2-13)$$

$$t_p = \frac{-2 \pm \sqrt{4 + \frac{8 V_p R}{F_o T_o}}}{2 \frac{R}{T_o}} \quad (2-14)$$

The reactor was operated as follows. A programming rate which would give the desired temperature range in a reasonable pyrolysis time was arbitrarily selected and the flow rate required to obtain the pyrolysis time so chosen calculated from Equation 2-13. The flows in the FGC system (Figure 2.16) were then adjusted so that the flow rate was as close as possible to the calculated value. The sample was then injected and the programming started within one

second by switching on the power sources (Figure 2.17). The reactor was not turned off until approximately twice the desired pyrolysis time had elapsed.

If the flow rate through the reactor were accurately set, the above procedure should result in the sample being swept through the reactor in the desired time, and thus exposed to the desired temperature range. However, even slight changes from the calculated flow would result in a temperature profile that was considerably different from what was expected, and therefore interpretation and comparison of results would be difficult.

The problems in the above method were in part due to leaving the reactor on for longer than the desired pyrolysis time. Since the flow could not be controlled accurately the temperature range that was experimentally obtained was often different from what had been calculated. However, switching off the reactor at the desired pyrolysis time creates similar problems. If the flow is not controlled accurately, and the reactor is switched off at the desired pyrolysis time the temperature range can be reduced or a varying profile of the type shown in Figure 2.19 can be obtained. This type of temperature profile is even less desirable than an extended temperature range, since it is more difficult to predict what the effect on the results would be.

It can be seen that temperature gradient reactor is more difficult to control than is a stepped temperature reactor, and accurate control is more critical since both

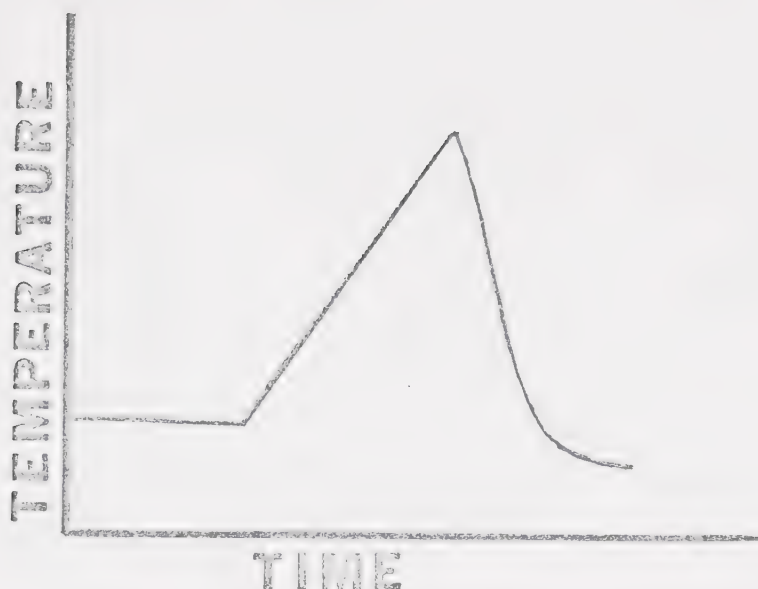


Figure 2.19 Temperature profile of a gradient reactor when programming is terminated before the sample has traversed the entire length of the reactor.

temperature and pyrolysis time depend on flow in a gradient reaction.

The term pyrolysis time is used to describe the time spent in a gradient reactor, since I prefer to use the term residence time only when the pyrolysis temperature is constant. The pyrolysis time is not as fundamental a parameter for a temperature gradient reactor as the residence time is for an isothermal reactor. The pyrolysis time gives an overall indication of the time the sample spends in the pyrolysis tube. However, during much of this time little reaction occurs, because the temperature is not high enough to cause pyrolysis. The programming rate is more indicative of the actual reaction conditions since it gives an idea of the time the sample spends any any one temperature.

Most of the problems encountered with the gradient reactor were due to the necessity of using fast programming rates so that a reasonably large temperature range could be covered without using excessively low flow rates. These problems could have been overcome more easily if the gradient reactor had been designed as such, rather than having been converted from the stepped temperature reactor.

3. RESULTS AND DISCUSSION

To test the effect of the various reactor configurations it was decided to use one compound to determine what changes, if any, occurred on changing reactors. A typical pyrogram of the compound chosen (2,3 - dimethylbutane) is shown in Figure 3.01. The size of the peaks in Figure 3.01 vary with temperature but usually all of the peaks shown can be detected (except at temperatures less than 550°C). However, if a peak was less than one percent of the largest peak it was considered negligible for the purpose of tabulation of results.

3.01 METHODS OF NORMALIZATION

To make meaningful comparisons of results from several chromatograms it is necessary to normalize the results. The method of normalization chosen can have a significant effect of the superficial appearance of the results, and in some cases could lead to false conclusions. There are three methods of normalization which yield useful comparisons and are readily calculated from the molar areas. These are,

$$\text{Normalized peak (M}_1\text{)} = \frac{\text{peak area}}{\text{sum of the areas of the product peaks}}$$

$$\text{Normalized peak (M}_2\text{)} = \frac{\text{peak area}}{\text{sum of the areas of product + reactant peaks}}$$

$$\text{Normalized peak (M}_3\text{)} = \frac{\text{peak area}}{\text{area of largest peak}}$$

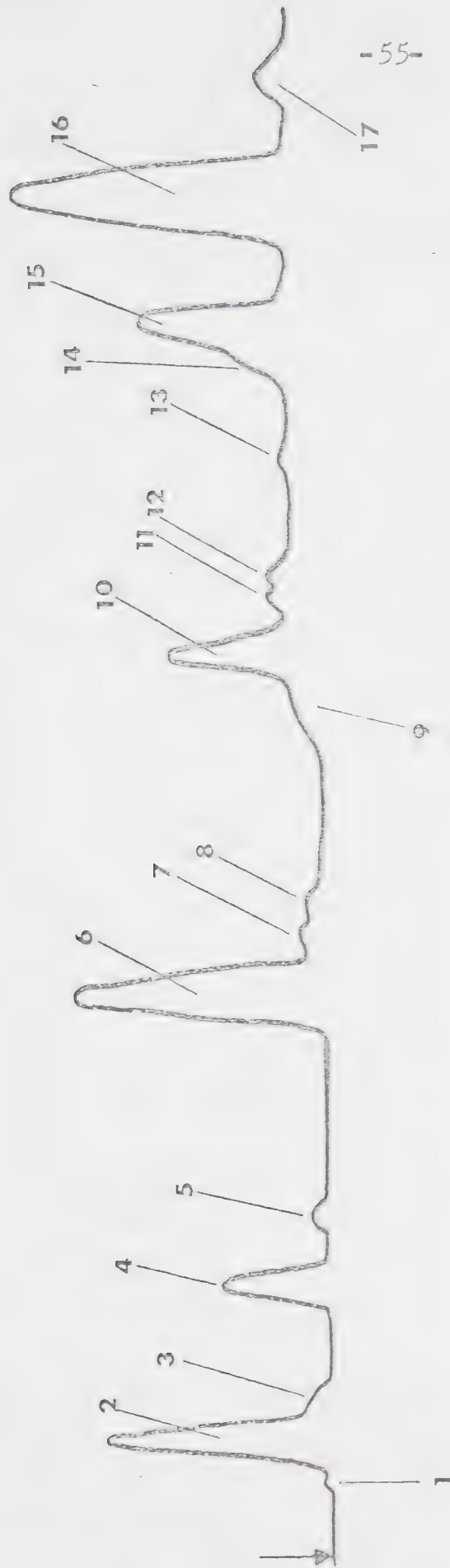


Figure 3.01 A typical pyrogram of 2,3-dimethylbutane

1. air
2. methane
3. carbon dioxide
4. ethylene
5. ethane
6. propylene
7. propane
8. propadiene

Grouped as
propylene+ in
tabulation of
results

9. water
10. isobutylene
11. 1,3-butadiene
12. 1-butene
13. trans-2-butene
14. cis-2-butene
15. 3-methyl-1-butene
16. isoprene
17. 2-methyl-2-butene
18. 2,3-dimethylbutane
19. 2,3-dimethyl-2-butene

Grouped as
isobutylene+
1,3-butadiene in results

Grouped together in
results only traces

Grouped as
2-methyl-2-butene in results

where all areas are the molar areas (corrected for variation in response factors).

From the definitions it is apparent that M_2 will approach M_1 as the extent of pyrolysis approaches one hundred percent. Table 3 shows the results of pyrolysis at several different temperatures with each of the three methods. Using the data obtained from one set of results only, it would be easy to draw varying conclusions on the effect of the temperature. For example, the results by method M_1 show the amount of methane formation as remaining almost constant over the entire temperature range, whereas, the results by methods M_2 and M_3 show a significant increase in the proportion of methane formed. Similarly M_1 shows the amount of 2-methyl-2-butene formed decreases steadily whereas the absolute amount increases. Method M_1 shows the product distribution best; however, since the amount of reactant is omitted from the normalization the results are not as generally useful as they could be. Method M_2 shows the total fragmentation pattern better, but comparisons are difficult to make since the reference point changes (the sum of the areas of the products + reactant becomes larger as the temperature increases). Method M_3 also has the disadvantage that the reference changes, however in my opinion, this method combines the best features of the previous two methods. Method M_3 is basically the same as the normalization method used in mass spectroscopy and is probably the most convenient method for specifying the fragmentation pattern for fingerprint files. In addition, M_3 is becoming the

TABLE 3 COMPARISON OF RESULTS OF PYROLYSIS USING DIFFERENT METHODS OF NORMALIZATION

products	550°C			600°C			625°C			645°C		
	M ₁	M ₂	M ₃	M ₁	M ₂	M ₃	M ₁	M ₂	M ₃	M ₁	M ₂	M ₃
methane	0.35	0.09	11	0.34	0.18	41	0.35	0.26	100	0.39	0.35	100
ethylene	0.02	--	--	0.03	0.02	4	0.06	0.05	18	0.10	0.09	25
ethane	--	--	--	--	--	1	0.01	--	2	0.01	--	3
propylene +	0.33	0.08	10	0.34	0.18	41	0.32	0.23	93	0.29	0.25	74
isobutylene + 1,3-butadiene	0.02	--	1	0.05	0.03	6	0.07	0.05	20	0.08	0.07	19
trans + cis 2-butene	--	--	--	0.01	0.01	1	0.02	0.01	5	0.01	0.01	3
2-methyl-2- butene +	0.28	0.07	9	0.22	0.12	26	0.16	0.12	45	0.10	0.09	24
2,3-dimethyl butane	XX	0.76	100	XX	0.46	100	XX	0.26	93	XX	0.11	31
2,3-dimethyl- 2-butene	--	--	--	--	--	--	--	--	--	--	--	1

XX - not included in normalization
 -- trace level or none

most common method of reporting pyrolysis data (10, 12). For these reasons the results in this thesis have been normalized using the third method (M₃). It is important however to check any conclusions by using the other methods of normalization, since the relative peak sizes are determined by the method used.

3.02 ISOTHERMAL OPERATION

The pyrolyzer was operated isothermally at several temperatures to obtain values to which the results from the stopped temperature and temperature gradient reactors could be compared. Table 4 shows the temperatures and residence times at which pyrolysis were carried out. Because the residence times varied somewhat the extent of reaction (α) also varied. Therefore, an attempt was made to adjust the α values to the median residence time of 6.8 seconds. This was done by assuming the pyrolysis approximately conformed to the rate equation for first order kinetics and therefore

$$1 - \alpha = e^{-k\tau} \quad (3-1)$$

where k is the rate constant, τ is the residence time and α is the extent of reaction.*

$$\alpha = \frac{\sum \text{molar areas of the products}}{\sum \text{molar areas of the products} + \sum \text{reactants}}$$

The adjusted α value was obtained by solving Equation 3-1 for k using the α value and the residence time; then substituting the median time of 6.8 seconds for τ and solving for a new α value (α'). A plot of the extent of reaction

as a function of temperature is given in Figure 3.02. The k values give an indication of the actual temperature at which the pyrolysis was carried out, and can be used to check whether two supposedly identical pyrolysis temperatures were actually identical. Using the rate constants it is also possible to calculate the extent of reaction that could be expected if the residence time was changed to some other value.

The results of the pyrolysis of 2,3-dimethylbutane can be seen in Table 5. There are several cases where the amounts of products formed at a specific temperature seem to be larger than the amounts of products formed at a slightly higher temperature. This is due to differences in the residence times, and therefore a different extent of reaction.

*The extent of reaction (pyrolysis) defined here is a convenient practical definition. It is not exactly equal to the percent reaction. For example, when α is equal to 0.5 less than half of the parent will have been pyrolyzed, since one mole of the parent will be converted into several moles of products on pyrolysis. To obtain the percent pyrolysis, it would be necessary to convert the molar areas to a relative number of carbon atoms. The percent of pyrolysis can be expressed more precisely as

$$\% \text{ pyrolysis} = \frac{\sum_{i=1}^{n-1} C_i A_{C_i}}{\sum_{i=1}^n C_i A_{C_i}} \cdot 100$$

where C_i is the number of carbon atoms, A_{C_i} is the sum of the molar areas of the peaks containing C_i atoms, and n is the number of carbon atoms in the parent compound.

TABLE 4 EFFECTS OF TEMPERATURE AND RESIDENCE TIMES ON THE ISOTHERMAL PYROLYSIS OF 2,3-dimethylbutane

Temperature	τ (sec)	α	$k \text{ sec}^{-1}$	α'
525°C A,B	7.9	0.15	2.05×10^{-2}	0.13
535 C	6.8	0.13	2.05×10^{-2}	0.13
545 D	6.0	0.15	2.71×10^{-2}	0.17
555 E	7.2	0.24	3.82×10^{-2}	0.23
555 F	6.7	0.24	4.10×10^{-2}	0.24
565 G	7.5	0.31	4.95×10^{-2}	0.28
575 H	7.0	0.31	5.30×10^{-2}	0.30
580 I	6.5	0.31	5.71×10^{-2}	0.32
580 J	5.8	0.29	5.90×10^{-2}	0.33
590 K	6.8	0.42	8.02×10^{-2}	0.42
595 L	7.3	0.50	9.55×10^{-2}	0.47
600 M	6.8	0.54	9.96×10^{-2}	0.54
625 N	7.0	0.75	1.98×10^{-1}	0.73
645 O	6.5	0.90	3.54×10^{-1}	0.91
520 °C	16.6	0.12	7.70×10^{-3}	
550	16.0	0.33	2.50×10^{-2}	
590	15.1	0.68	7.55×10^{-2}	
615	14.8	0.79	1.06×10^{-1}	

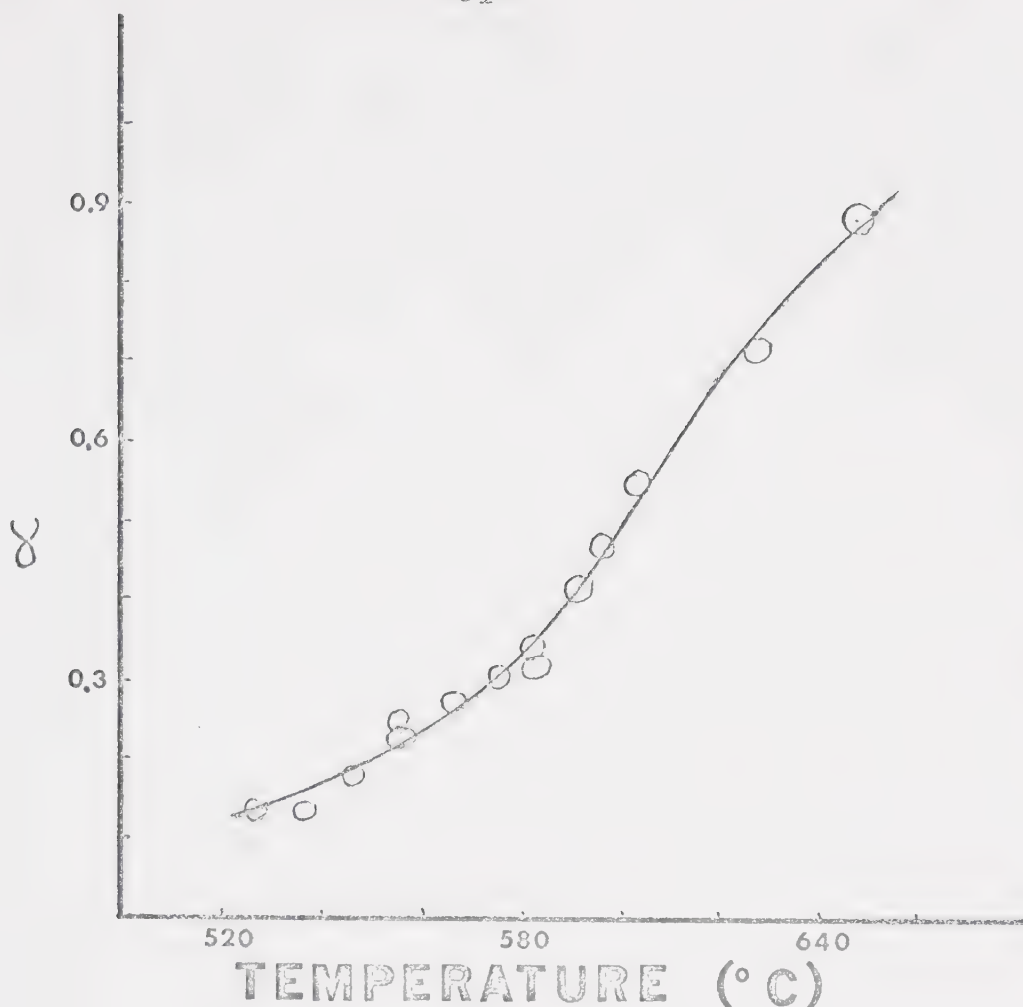


Figure 3.02 Extent of reaction (α) as a function of temperature for 2,3-dimethylbutane.

The three main products of pyrolysis are methane, propylene, and 2-methyl-2-butene. Of these, only propylene and 2-methyl-2-butene can be considered characteristic of the parent molecule, and are therefore useful for identification of the parent. These compounds are formed at all temperatures, however, at temperatures less than 580°C these products are formed almost exclusively. This would indicate that the pyrolysis should be carried out at these lower temperatures except that the extent of reaction is also low (less than about 30%); therefore the reaction is not as complete as desired.

TABLE 5 PYROLYSIS YIELDS OF 2,3-dimethylbutane AT VARIOUS TEMPERATURES - MEDIAN RESIDENCE TIME = 6.8 SECONDS

Temperature of products	525 A	525 B	535 C	545 D	555 E	555 F	565 G	575 H	580 I	580 J	590 K	595 L	600 M	625 N	645 O
methane	7	6	5	7	11	11	15	15	16	14	25	33	41	100	100
ethylene	---	---	---	---	1	1	1	1	1	1	1	3	4	19	25
ethane	---	---	---	---	---	---	---	---	---	---	---	1	1	2	3
propylene +	5	6	5	6	10	10	15	15	16	14	24	33	41	93	74
isobutylene + 1,3-butadiene	---	---	---	---	1	1	1	1	1	1	2	6	6	20	19
trans + cis 2-butene	---	---	---	---	---	---	---	---	---	---	1	1	1	5	3
2-methyl-2-butene +	6	6	5	6	9	9	13	12	12	11	19	23	26	45	24
2,3-dimethyl butane	100	100	100	100	100	100	100	100	100	100	100	100	100	98	31
2,3-dimethyl-2-butene	---	---	---	---	---	---	---	---	---	---	---	---	---	---	1

-- trace level or none; Letters(A,B,etc) refer to Table 4 in this table only.

Considering a combination of extent of pyrolysis and the fragmentation pattern, the best conditions for pyrolysis with this reactor, are a temperature of 600°C to 625°C and a residence time of seven seconds. This gives a fragmentation pattern in which the most characteristic peaks are large, and the extent of reaction is within the range 0.50 to 0.75. Above 625°C the secondary reactions increase strongly as evidenced by the increased methane and ethylene formation and the decreased formation of 2-methyl-2-butene and propylene at 645°C as compared to 625°C. There is also considerable increase in both the amount and number of other secondary products.

Table 6 shows some results obtained by varying the temperature and the residence time. It can be seen that just increasing the residence time does not improve the pyrolysis pattern as much as increasing the pyrolysis temperature at the same residence time (compare A, B, C, and C, D, E). Although D and E show approximately the same extent of pyrolysis the pattern in E is more useful for characterization since the most characteristic peaks are larger in E. However it is also apparent that long times and medium temperatures (570 to 600°C) give a better pyrolysis pattern than short times and high temperatures (compare the amount of 2-methyl-2-butene formation in runs G and H). The combination of long residence times with relatively high temperatures, however, can yield results that are not as useful as those obtained at higher temperatures and shorter times. An example of this can be seen in the

pyrolysis patterns of runs D, E, and F. Run F shows less formation of propylene and 2-methyl-2-butene than run E and a considerable increase in the formation of methane and ethylene as compared to run D. It is therefore clear that there is only a short range of temperatures and residence times in which a compound can be pyrolyzed to give the best pyrogram and the largest extent of reaction. This agrees with

TABLE 6 PYROLYSIS PATTERN OF 2,3-dimethylbutane AT VARIOUS TEMPERATURES AND RESIDENCE TIMES

Temperature °C	555	550	590	590	625	615	585	645
τ (sec)	6.7	16.6	6.8	15.1	7.0	14.8	26.3	6.5
products	A	B	C	D	E	F	G	H
methane	11	17	25	78	100	100	100	100
ethylene	1	1	1	12	18	19	23	25
ethane	--	--	--	1	2	2	3	3
propylene +	10	17	24	65	93	77	70	75
isobutylene + 1,3-butadiene	1	1	2	14	20	19	20	19
trans + cis 2-butene	--	--	1	2	5	3	2	3
2-methyl-2- butene +	9	13	19	38	45	37	46	24
2,3-dimethyl butane	100	100	100	100	98	69	41	31
2,3-dimethyl- 2-butene	--	--	--	--	--	3	1	1
extent of reaction (α)	0.24	0.33	0.42	0.68	0.75	0.79	0.86	0.90

-- trace level or none

the conclusions of Sutton and Harris (28) who advised using long residence times and as low a temperature as possible to achieve the desired extent of pyrolysis.

3.03 STEPPED TEMPERATURE OPERATION

Table 7 shows some results for the pyrolysis of 2,3-dimethylbutane in a stepped temperature reactor. Two runs were made operating the reactor isothermally (A and B) to give a reactor with a residence time of about 26 seconds. Several runs were then made with the reactor operated in the stepped mode with the temperatures of the tubes such that a weighted average of the temperatures was approximately equal to the isothermal temperatures in runs A and B. The weighted average was obtained by multiplying the temperature and the residence time of each tube, adding the temperature-time products and dividing by the total residence time.

Comparing the isothermal run at 585°C with runs B, C, D, E, and F the most significant difference is the large difference in the amount of 2-methyl-2-butene formed. The reason for this is illustrated in Run G which is the pyrolysis pattern for 2-methyl-2-butene under the same conditions as run E. In run G, 2-methyl-2-butene is pyrolyzing considerably under the conditions of reaction and therefore a significant proportion of what was thought to be the pyrolysis pattern of 2,3-dimethylbutane results from the secondary reaction of the product 2-methyl-2-butene.

TABLE 7 PYROLYSIS PATTERN OF 2,3-dimethylbutane IN A STEPPED TEMPERATURE REACTOR

products	A	B	C	D	E	F	G
methane	100	100	100	100	100	100	89
ethylene	23	29	30	38	36	29	30
ethane	3	3	4	3	5	2	--
propylene +	70	62	82	55	66	70	13
isobutylene + 1,3-butadiene	20	19	25	18	21	21	46
trans + cis 2-butene	3	3	4	2	3	2	4
2-methyl-2- butene +	46	19	25	13	18	27	100*
2,3-dimethyl butane	41	20	25	12	17	42	XX
2,3-dimethyl- 2-butene	1	1	1	3	2	1	XX
extent of reaction (α)	0.86	0.92	0.92	0.95	0.94	0.86	0.69

* parent

total residence times and temperatures are listed in the following order -- τ , P_1, P_2, P_3, P_4 , T_{average}

A -- 26.3, 585, 585, 585, 585.

B -- 25.9, 600, 600, 600, 600.

C -- 25.8, 585, 585, 595, 625, 597.

D -- 25.5, 570, 590, 615, 645, 607.

E -- 26.3, 540, 565, 600, 625, 585.

F -- 26.5, 535, 560, 595, 620, 580.

G -- 26.5, 535, 560, 595, 620, 580.

(2-methyl-2-butene

Looking back at Table 5 it is apparent that the amount of isobutylene and 1,3-butadiene formed increases considerably and abruptly above 600°C. Since isobutylene is not a product that would be expected from the pyrolysis of 2,3-dimethylbutane (by the Rice-Kossiakoff theory) (19) and 1,3-butadiene should not be obtained in major proportions, the 2-methyl-2-butene formed from 2,3-dimethylbutane starts to undergo reaction itself at this temperature. It could be expected that the reaction curve would resemble that of Figure 3.02 and a strong increase could be expected over a small range of temperature. The hoped for advantage of a stepped reactor, that is, the expectation that products once formed would not react further does not in fact occur.

However, the data in Table 7 does show some useful purpose for a stepped temperature reactor. Comparing runs B (isothermal at 600°C), C ($T_{av} = 597^\circ\text{C}$) and D ($T_{av} = 607^\circ\text{C}$) it can be seen that the pyrolysis pattern from C is the most characteristic of the three and yet the extent of reaction is high. This is because about half of the pyrolysis is carried out at a temperature of 585°C. This tends to indicate that a stepped temperature reactor with a narrow range can give better results than a stepped reactor with a wide temperature range. One feature that must be considered a disadvantage of this type of reactor is the considerable difference in pyrolysis pattern that can result when conditions are varied only slightly. Runs E and F were carried out under conditions that varied only slightly yet the

pyrolysis patterns are considerably different. It must therefore be concluded that obtaining reproducibility with a stepped temperature reactor would require precise control of temperature and residence time since the number of separate adjustments that must be made are larger (in this case four tubes must be adjusted not just one).

An ideal reactor would yield maximum information and still be versatile. The stepped temperature reactor is not an efficient reactor for the pyrolysis of a specific compound but it is versatile. Table 8 shows the results obtained from the pyrolysis of the isomers of C_6H_{14} . Even without specifically identifying the individual products of pyrolysis it is possible to distinguish between the isomers, and to identify the parent. From a knowledge of the Rice-Kossiakoff theory of pyrolysis (19, 30) it is possible to predict what products would be formed upon pyrolysis. Table 9 gives the carbon skeletons of the isomers of C_6H_{14} and the major products that would be expected in each case. Looking at Table 8, it is apparent that two of the runs (A, B) yield significantly more three carbon compounds than the other runs. 2-methylpentane should yield more two carbon and four carbon compounds, and fewer five carbon compounds than 2,3-dimethylbutane. Considering this, A can be identified as 2,3-dimethylbutane and B as 2-methylpentane. Comparing the remaining runs, C has a significantly larger amount of four carbon compounds than the others, however run D also shows a considerable amount of four carbon atoms. Since the

only compounds that would be expected to produce four carbon compounds in large amounts on pyrolysis are 3-methylpentane and 2,2-dimethylbutane, the lack of four carbon compounds in E identifies E as n-hexane. This identification is further confirmed by the large amount of two carbon compounds (ethylene + ethane) in run E. Runs C and D can be differentiated by the proportions of two, three, and four

TABLE 8 PYROLYSIS PATTERN OF ISOMERS OF C_6H_{14}

pyrolysis products	A	B	C	D	E
C_1	100	100	100	100	54
C_2	30	76	57	79	107*
C_3	71	63	11	35	36
C_4	23	35	47	34	13
C_5	27	6	15	10	1
C_6	42	68	54	40	56
∞	0.86	0.81	0.81	0.87	0.79

* ethylene + ethane , ethylene = 100

Reaction conditions: $P_1(540^\circ C)$ $P_2(565)$

$P_3(600)$ $P_4(625)$; total residence time = 26.3 sec

A. 2,3-dimethylbutane B. 2-methylpentane

C. 2,2-dimethylbutane C. 3-methylpentane,

E. n-hexane

carbon compounds formed. Run D shows larger amounts of two carbon compounds than run C. Run C shows a large amount of four carbon compounds. It is difficult to obtain three carbon compounds from 2,2-dimethylbutane since the most likely fragmentation is the one indicated in Table 9. However, three carbon compounds can be obtained from 3-methylpentane by secondary reactions (3-methylpentane \rightarrow 2-methyl-1-butene \rightarrow propylene). From the relative proportions of three carbon compounds it is thus possible to identify C as 2,2-dimethylbutane, and D as 3-methylpentane;

From the above it can be seen that these hydrocarbons

TABLE 9 ISOMERS* OF C_6H_{14} AND THEIR MAJOR PYROLYSIS PRODUCTS**

<u>PARENT</u>		<u>PRODUCTS</u>
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	\longrightarrow	$\begin{array}{c} \text{C} \\ \\ \text{C}=\text{C} \\ \\ \text{C} \end{array} + \text{C}=\text{C}$
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	\longrightarrow	$\text{C}-\text{C}=\text{C} + \begin{array}{c} \text{C}-\text{C}=\text{C}-\text{C} \\ \\ \text{C} \end{array}$
$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	\longrightarrow	$\text{C}-\text{C}=\text{C} + \text{C}=\text{C} + \begin{array}{c} \text{C} \\ \\ \text{C}=\text{C} \\ \\ \text{C} \end{array}$
$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	\longrightarrow	$\text{C}=\text{C} + \text{C}-\text{C}=\text{C}-\text{C}$
$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$	\longrightarrow	$\text{C}=\text{C} + \text{C}-\text{C}=\text{C}$

* Only the carbon skeletons are shown

** By the Rice-Kossiakoff theory (19)

can all be pyrolyzed at the same stepped temperature conditions and yield useful results. The stepped reactor is thus probably most useful for fingerprint analysis and for distinguishing one compound from another. The method of organizing the results in Table 8 is useful only if the general identity of the parent compounds is known. It would be difficult, for example, to differentiate between an alkane and an alkene without identifying the individual peaks. However it might be possible to use a system such as that used by Fanter, Walker and Wolf (10) of grouping the products according to retention index to yield a more useful pattern for fingerprint analysis.

The biggest advantage of using a temperature range in a reactor is the versatility that the range produces. This versatility is further illustrated in Table 10, which gives the results of pyrolysis of several oxygenated compounds. Sutton and Harris (29) determined that the optimum pyrolysis temperatures for these compounds were:

ethyl acetate	420 to 520°C
methyl ethyl ketone	540 to 640°C
diethyl ether	520 to 660°C

Pyrolyses were carried out at the following sets of temperatures;

Runs A, B, C, D		Runs E, F, G, H, I	
P ₁ 480°C	P ₂ 530°C	P ₁ 480°C	P ₂ 530°C
P ₃ 585°C	P ₄ 640°C	P ₃ 585°C	P ₄ off

Runs A, B, C, and D show a high extent of pyrolysis and sufficient characterization to be able to identify the parent

TABLE 10 PYROLYSIS PATTERNS OF OXYGENATED COMPOUNDS IN A
STAGED THERMAL DECOMPOSITION REACTION*

products	A	B	C	D	E	F	G	H	I
carbon monoxide	57	53	73	9	1	2	1	6	N.S.
methane	54	75	100	24	1	2	2	9	10
carbon dioxide	6	N.S.	N.S.	49	--	--	--	2	19
ethyl mo	100	100	97	100	6	11	10	9	100
ethane	16	18	9	N.S.	3	2	3	1	
propylene +	2	4	10	1				--	--
acetaldehyde	29	20		8	5	8	9		--
ethanol	--	--	--	7					--
propionaldehyde + vinyl methyl ketone								1	
divinyl ether + vinyl ethyl ether	2	5							
acetic acid				5					5
diethyl ether (parent)	99	35			100	100	100		
methyl ethyl ketone (parent)			95					100	
ethyl acetate (parent)				8					12
extent of reaction	0.73	0.88	0.78	0.96	0.14	0.20	0.20	0.22	0.92

*Results have not been converted to molar areas before

normalization

-- trace, N.S. not separated from other peaks

compounds. However, the reproducibility of the runs is poor. Runs A and B were supposedly carried out at the same conditions but the pyrolysis pattern is not reproduced. This again illustrates the need for careful control if reproducibility is to be obtained. The runs at the lower temperatures (E, F, G, H, I) are not useful for the identification of the parent since the peaks are small and therefore hard to identify. The small peaks can be attributed to the low extent of pyrolysis.

The products found in these runs differed considerably from the products found by Sutton and Harris (29). Extreme differences were also found in the products and product distribution with the stepped reactor on changing the temperature and the number of steps used (Table 11). The products formed at 480°C agree with those found by Sutton and Harris, however the products formed at the higher temperatures differ considerably. Since the extent of pyrolysis is 0.89 after P_2 it is likely that the difference in pyrolysis pattern is due to secondary reactions and possibly a different mechanism of reaction at the higher temperatures.

3.04 TEMPERATURE GRADIENT OPERATION

Table 12 shows some results obtained by operating pyrolysis tube P_{14} as a temperature gradient reactor and programming at several different rates. One important difference in the runs can be noticed on comparing runs

TABLE 11 VARIATION IN THE PYROLYSIS PATTERN OF ETHYL ACETATE WITH TEMPERATURE *

products	A	B	C	D
carbon monoxide	--	--	--	9
methane	--	1	10	24
carbon dioxide	--	4	19	49
ethylene	21	100	100	100
propylene +	--	--	--	2
acetaldehyde	--	--	--	8
ethanol	--	--	--	7
acetic acid	1	1	5	5
ethyl acetate	100	14	12	8
extent of reaction	0.18	0.89	0.92	0.96

* Results have not been converted to molar areas before normalization.

Temperatures of steps in the stepped reactor are given in the following order - P₁, P₂, P₃, P₄. (°C)

A. 480, off, off, off, C. 480, 530, 585, off,
 B. 480, 530, off, off, D. 480, 530, 585, 640,

TABLE 12 PYROLYSIS PATTERN OF 2,3-dimethylbutane IN A
GRADIENT REACTION

Initial T °C Final T °C R °C/sec t _p sec	Products									
	A	B	C	D	E	F	G	H	I	J
methane	100	100	100	100	100	100	100	100	86	4
ethylene	39	47	47	46	47	36	30	26	16	--
ethane	3	3	4	3	3	3	2	2	1	--
propylene +	33	15	27	28	27	45	64	75	70	3
isobutylene + 1,3-butadiene	8	4	9	8	6	13	18	23	16	--
trans + cis 2-butene	8	4	9	8	6	13	18	23	16	--
2-methyl-2- butene +	4	1	3	3	3	9	20	31	38	4
2,3-dimethyl butane	3	4	5	6	9	17	39	59	100	100
2,3-dimethyl- 2-butene	9	9	9	9	8	7	6	3	--	--
extent of reaction (α)	0.99	0.98	0.98	0.97	0.96	0.93	0.86	0.82	0.71	0.10

H, I, and J. Runs H and I were obtained by programming the reactor for thirty seconds, but relying on the flow through the pyrolysis tube to carry the sample through the reactor in the desired pyrolysis time (about 17 seconds). Run J was obtained by turning the reactor off after programming for sixteen seconds. Since the pyrolysis time in runs H and I is supposedly seventeen seconds, little difference should have been detected among runs H, I, and J. The probable reason for the difference is that the flow rate is lower than what was calculated and thus the pyrolysis times for H and I are longer (and therefore the final temperature is higher) than what was calculated. This is further confirmed by comparing run J (Table 12) and run A (Table 13). The pyrolysis patterns from these two runs are comparable.

The difference noted above between the calculated times and temperatures, and the actual times and temperatures is due to the difficulty in controlling the flow rate through the pyrolysis tube accurately. A change in the flow rate of ten percent can result in a change in the temperature of about about ten degrees, even at the lowest programming rates (see Appendix). Since the flow at the entrance to the pyrolyzer (F_0) was only 3.7 ml/min, a change of ten percent is only 0.4 ml/min. With the experimental apparatus used, it was extremely difficult to control or to reproduce the flow rates within ten percent, therefore the uncertainty in the temperatures could be as high as thirty to forty

degrees. It was also noticed that the flow error was usually a lower flow rate than the set value, (as read from the rotameter and calibration chart - see Appendix), therefore the final temperature would usually be higher than the calculated value.

Even if the temperature ranges are not known accurately

TABLE 13 PYROLYSIS PATTERN OF 2,3-dimethylbutane AT SEVERAL TEMPERATURES - MEDIAN RESIDENCE TIME = 15.6 SECONDS

Temperature °C	520	550	590	615
τ (sec)	16.6	16.0	15.1	14.8
products	A	B	C	D
methane	5	17	78	100
ethylene	--	1	12	19
ethane	--	--	1	2
propylene +	4	17	65	77
isobutylene + 1,3-butadiene	--	1	14	19
trans + cis 2-butene	--	--	2	3
2-methyl-2- butene +	4	13	38	37
2,3-dimethyl butane	100	100	100	69
2,3-dimethyl- 2-butene	--	--	--	3
extent of reaction (α)	0.12	0.33	0.68	0.79

several trends can still be noted from the results. A high program rate combined with a relatively high (500°C) starting temperature yields results that are useless for characterization since the products are almost entirely simple molecules. The results obtained using a lower initial temperature (450°C) are only slightly better. The use of a high program rate results in a final temperature so high that secondary reactions predominate, and should therefore be avoided.

The results become more useful as the programming rate is reduced. The results obtained at a rate of $4.6^{\circ}\text{C}/\text{sec}$. (H, I - Table 12) are as useful for characterization as those obtained isothermally at 585°C and a residence time of 26 seconds, (A - Table 7) and the extent of reaction is only slightly less.

Runs H and I (Table 12) were supposedly obtained at the same pyrolysis conditions. However, the conditions must have been different, since the pyrolysis patterns are noticeably different. This difference is again due to the difficulty in reproducing the flow accurately.

Comparing run H with the results obtained operating pyrolysis tube P_{14} isothermally (Table 13), it can be seen that the results from the gradient reactor show a larger extent of pyrolysis at a lower temperature than the results obtained from the isothermal reactor. For example, run H

(Table 12) shows about the same extent of pyrolysis as run D (Table 13) and approximately the same pyrolysis pattern. Since run D was obtained at a temperature of 615°C and a residence time of fifteen seconds it should not compare with results obtained by programming from 450°C (to about 530°C at a rate of $5^{\circ}\text{C}/\text{sec}$) unless the pyrolysis times for the gradient reactor are greatly in error, and such a large error is unlikely. One speculation could be that the mechanism of reaction is changed by the rapidly increasing temperature and the gradient reactor therefore yields a higher extent of pyrolysis by incorporating a temperature range than is obtained by an isothermal reactor operating at a higher temperature.

Another explanation is that there is a large error in the operation of the thermocouple (due to a finite heat capacity - see Section 2.05) and the programming rates are actually higher than they appear to be. A combination of errors (higher program rate and longer pyrolysis times) might make the final temperature high enough to account for the observed similarity between the above runs, but large errors in both programming rate and pyrolysis time would be required. More investigation is needed using a system in which the flow rate can be accurately controlled, and the temperature monitored continuously, to determine if the runs obtained from the gradient reactor are valid, and the reasons for the observed similarity between runs D and H.

Table 14 shows the results obtained from the pyrolysis of diethyl ether and ethyl acetate in the gradient reactor. A comparison is also made with the results obtained from the stepped temperature reactor. Again it is apparent that more simple products are formed in the gradient reactor at the same extent of pyrolysis. No rates lower than those indicated were tried so it is not possible to evaluate the effect of lowering the programming rate.

3.05 GOLD TUBING REACTOR

Much research in pyrolysis gas chromatography has been directed towards improving reactor performance and the reproducibility of the pyrolysis pattern. Reactors of many different materials (glass, quartz, platinum, stainless steel, gold, silver) have been constructed and used with varying success (20). Cramers (2) recommends gold as the best metal for the construction of reactors. He found that the products formed in a gold reactor are closer to those predicted theoretically (19) than the products formed in other reactors. Fanter, Walker and Wolf (10) have also used gold reactors and discussion at a recent symposium (12) gives the impression that gold is the best reactor material.

Two gold tubing reactors were therefore constructed, so that the results from gold reactors could be compared with the results obtained from quartz reactors. Details of the construction of the gold reactors can be found in the Appendix. Table 15 lists the temperatures and the

TABLE 14 PYROLYSIS PATTERN OF OXYGENATED COMPOUNDS IN A GRADIENT REACTOR*

products	A	B	C	D	E
carbon monoxide	65	78	53	20	9
methane	100	94	75	41	24
carbon dioxide	N.S.	N.S.	N.S.	54	49
ethylene	93	100	100	100	100
ethane	13	22	18	--	--
propylene +	2	3	4	5	1
acetaldehyde	2	10	20	--	8
ethanol	2	2	--	3	7
divinyl ether + vinyl ethyl ether	N.S.	N.S.	5		
acetic acid				4	5
diethyl ether(parent)	26	31	36		
ethyl acetate(parent)				24	8
extent of reaction	0.92	0.91	0.88	0.90	0.96

* Results have not been converted to molar areas before normalization.

-- trace, N.S. not separated from other peaks

Conditions of reaction:

A. $T_0 = 500^\circ\text{C}$, $R = 8.3^\circ\text{C}/\text{sec}$, range 500 to 630°C .

B. $T_0 = 450^\circ\text{C}$, $R = 9.0^\circ\text{C}/\text{sec}$, range 450 to 600°C .

C & E. Stepped P_1 (480°C), P_2 (530), P_3 (585), P_4 (640)

D. $T_0 = 450^\circ\text{C}$, $R = 9.0^\circ\text{C}/\text{sec}$, range 450 to 600°C .

TABLE 15 TEMPERATURES AND RESIDENCE TIMES FOR GOLD TUBING REACTORS

	Temp °C	τ sec	α	α' at 14.2 sec	k (sec ⁻¹) for gold tubing	k(sec ⁻¹)/time/temp for quartz (3.8mm)
3 mm tubing	520	15.4	0.06	0.06	4.02×10^{-3}	$7.70 \times 10^{-3}/16.6/520$
	540	15.0	0.13	0.12	9.29×10^{-3}	$2.50 \times 10^{-2}/16.0/550$
	560	14.7	0.32	0.31	2.63×10^{-2}	
	580	14.3	0.49	0.49	4.70×10^{-2}	
	600	14.0	0.71	0.72	3.84×10^{-2}	$7.55 \times 10^{-2}/15.1/590$
	620	13.7	0.85	0.86	1.38×10^{-1}	$1.06 \times 10^{-1}/14.8/615$
	640	13.4	0.95	0.96	2.24×10^{-1}	
	660	13.1	0.99	1.00	3.51×10^{-1}	
1 mm tubing	540	5.8	0.04		7.04×10^{-3}	$2.71 \times 10^{-2}/6.0/545$
	580	5.6	0.19		3.76×10^{-2}	$5.71 \times 10^{-2}/6.5/580$
	600	5.4	0.35		7.96×10^{-2}	$9.96 \times 10^{-2}/6.8/600$
	620	5.3	0.55		1.51×10^{-1}	$1.98 \times 10^{-1}/6.8/625$
	640	5.2	0.71		2.33×10^{-1}	$3.54 \times 10^{-1}/6.5/645$
	660	5.1	0.86		3.85×10^{-1}	
	680	5.0	0.94		5.63×10^{-1}	

residence times at which pyrolysis was done using the gold tubing reactors. The k and α' values were calculated as they were in Section 3.02. The k values of the gold tubing are sufficiently different from those in quartz to result in different extents of pyrolysis at similar temperatures. As can be seen by comparing the data in Tables 16 and 17 the extent of pyrolysis in gold tubing is less than that in quartz at the same temperature. The gold tubing reactor requires a higher temperature to achieve the same extent of pyrolysis. This is especially true at the lower temperatures and shorter residence times. At the higher temperatures and longer residence times the extent of reaction becomes similar at similar temperatures (as do the k values). Comparing results at the same extent of pyrolysis, it can be seen that there is little difference in the pyrolysis patterns even though the temperatures are different.

It is important to note that although the residence times of the gold and quartz reactors in Table 16 are approximately the same, the gold tubing is 1 mm in diameter and the quartz tubing is 3.8 mm in diameter. Since the pyrolysis patterns obtained from both reactors are similar at high temperatures and longer times (Table 17) it is possible that the differences observed in Table 16 are partially due to the differences in tube diameter--the smaller diameter tube (larger surface area to volume ratio) inhibits the reaction of the free radicals formed, because of more frequent collisions with the walls of the tube.

TABLE 16 COMPARISON OF THE PYROLYSIS PATTERN OF 2,3-DIMETHYLBUTANE
IN 1 mm GOLD TUBING AND QUARTZ TUBING**

Products	Temperature °C τ sec		Au*		Qtz*		Au		Qtz		Au		Qtz		Au		Qtz		Au		Qtz		Au		Au	
			540	535	530	590	600	600	620	625	640	645	660	680												
methane	2	5	8	16	19	41	45	100	89	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ethylene	---	---	---	1	1	4	4	18	14	25	23	30	30	30	---	---	---	---	---	---	---	---	---	---	---	---
ethane	---	---	---	---	---	1	---	2	1	3	4	5	5	5	---	---	---	---	---	---	---	---	---	---	---	---
propylene +	1	5	7	16	19	41	42	93	85	75	87	66	66	66	---	---	---	---	---	---	---	---	---	---	---	---
isobutylene + 1,3-butadiene	---	---	---	1	1	6	5	20	15	19	19	21	21	21	---	---	---	---	---	---	---	---	---	---	---	---
trans + cis 2-butene	---	---	---	---	---	1	1	5	3	3	3	4	4	4	---	---	---	---	---	---	---	---	---	---	---	---
2-methyl-2- butene +	1	5	7	12	15	26	27	45	42	24	31	16	16	16	---	---	---	---	---	---	---	---	---	---	---	---
2,3-dimethyl butane	100	100	100	100	100	100	100	98	100	31	45	17	17	17	---	---	---	---	---	---	---	---	---	---	---	---
2,3-dimethyl- 2-butene	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
extent of reaction (x)	0.04	0.13	0.19	0.31	0.35	0.54	0.55	0.75	0.71	0.90	0.86	0.94	0.94	0.94	---	---	---	---	---	---	---	---	---	---	---	---

* Au - gold tubing, Qtz - quartz tubing ** quartz tubing is 4mm i.d.

TABLE 17 COMPARISON OF THE PYROLYSIS PATTERNS OF 2,3-dimethylbutane
IN 3mm GOLD TUBING AND QUARTZ TUBING

Temperature °C τ (sec)	Au 520 15.4	Qtz 520 16.6	Au 540 15.0	Au 560 14.7	Qtz 550 16.0	Au 580 14.3	Au 600 14.0	Qtz 590 15.1	Au 620 13.7	Qtz 615 14.8	Au 640 13.4	Au 660 13.1
products												
methane	2	5	5	17	17	35	94	78	100	100	100	100
ethylene	--	--	--	1	1	3	12	12	20	19	23	35
ethane	--	--	--	--	--	--	1	1	2	2	4	5
propylene +	2	4	5	15	17	33	79	65	77	77	59	42
isobutylene + 1,3-butadiene	--	--	--	1	1	4	17	14	20	19	15	12
trans + cis 2-butene	--	--	--	--	--	--	3	2	5	3	2	2
2-methyl-2- butene +	2	4	5	13	13	23	43	33	30	37	14	5
2,3-dimethyl butane	100	100	100	100	100	100	100	100	46	69	12	3
2,3-dimethyl- 2-butene	--	--	--	--	--	--	--	--	3	3	3	6
extent of reaction (%)	0.06	0.12	0.13	0.32	0.33	0.49	0.71	0.68	0.85	0.79	0.95	0.99

* Quartz tubing is 4 mm i.d.

Figure 3.03 shows a plot of the rate constants of the gold and quartz reactors as a function of temperature. It can be seen that the rate constants for the quartz reactor with a residence time of about 16 seconds, are lower than the rate constants of the quartz reactor with a residence time of about 7 seconds. With the gold reactor, the rate constants for the reactor with a residence time of about 14 seconds (3 mm tubing) are higher than the rate constants for the reactor with a residence time of about 5 seconds (1 mm tubing) up to approximately 610°C. This tends to confirm the possibility that there is a significant effect due to the differences in tube diameter.

However, it is likely that the differences in Table 16 are due to other factors or a combination of factors since above 610°C the rate constants for the gold tubing reactor are higher for the shorter residence times than are the rate constants for the quartz reactor (where the tube diameter is the same for reactors of both residence times).

For example, the pressure and the flow rate could also have a significant effect. At high pressures, diffusion is lower so there is less chance of a free radical diffusing to the wall to the pyrolysis tube. If a sample is injected into a pyrolyzer with a high flow rate, the number of inert molecules surrounding each sample molecule will be greater than if the sample had been injected into a pyrolyzer with a low flow rate. If the number of inert molecules is greater, diffusion will similarly be lower and there will



Figure 3.03 Rate constants in gold and quartz tubing reactors as a function of temperature. 1. Quartz, $\tau = 7 \text{ sec}$. 2. Gold (1 mm) $\tau = 5 \text{ sec}$. 3. Gold (3 mm) $\tau = 14 \text{ sec}$. 4. Quartz $\tau = 16 \text{ seconds}$

be less chance of a free radical diffusing to the wall during its lifetime. Since the time required for thermal equilibration is also the time required for a molecule to travel a distance approximately equal to the radius of the tube, the diameter of the tube would also be expected to have an effect of the rate constant.

3.06 SUMMARY

From the previous sections it is concluded that an isothermal reactor gives the best results for the pyrolysis of a specific compound. Furthermore, an isothermal reactor has the advantage that it is easily controlled. However, since there is only a small range in which any compound can be pyrolyzed to give the most useful information it is necessary to make frequent adjustment of temperature and residence time to obtain optimum conditions. These adjustments require a prior knowledge of the identity of the compound to be pyrolyzed. Since one temperature can not be used to pyrolyze a large range of compounds the usefulness and versatility of an isothermal reactor in a PGC system is limited.

A reactor incorporating a temperature range is versatile, but the results obtained are not as useful for the exact identification of an unknown compound as the results obtained from an isothermal reactor. This type of reactor however, can be useful for fingerprint analysis and distinguishing

closely related compounds. It could also be used to gain an idea of the identity of a compound so that more careful pyrolysis could be done in an isothermal reactor.

A stepped temperature reactor is relatively easy to construct and the results obtained are useful. However, it is extremely difficult to control, especially if a wire wound tube is used as the basic pyrolysis unit. The reliability and reproducibility of the reactor could be improved if the temperature of each step could be monitored individually and continuously. This, however is difficult in a wire wound reactor. The use of several pyrolysis tubes also increases the pre-column dead space considerably and therefore necessitates the use of more drastic programming conditions with the analytical column to obtain good resolution.

The temperature gradient reactor is probably the most versatile type of reactor of the three types used. The results obtained by operating the reactor at low programming rates compare favorably with the results from the isothermal reactor. However, the results are not conclusive, and further work is required to determine if the results are valid. Because of the versatility of this type of reactor, it would be desirable to know if the results obtained under optimum conditions were comparable to those obtained from the isothermal reactor.

The results from the gold tubing reactors tend to indicate that the pyrolysis pattern obtained from gold

tubing is not much different than the pattern obtained from quartz at the same extent of pyrolysis. This is contrary to the conclusions of Cramers but the difference can possibly be attributed to the fact that Cramers' pyrolyses were done at less than ten percent pyrolysis whereas the results obtained in this study were extents of pyrolysis ranging from ten to about one hundred percent.

Several comments can be made about the design of the reactors used in this thesis. First, a wire wound reactor is undesirable since it is difficult to control, is not uniform and does not yield the best temperature profiles. The ease with which it can be constructed does not overcome these disadvantages. Furthermore, the temperature of any pyrolyzer should be able to be monitored continuously under operating conditions if the actual reaction conditions are to be known. Monitoring the temperature of a wire wound reactor is difficult. I therefore recommend that wire wound reactors be avoided where precise control of the temperature is essential.

3.07 SUGGESTIONS FOR FURTHER WORK

Several possible areas for further work can be seen from the results and conclusions in the previous sections. The reproducibility and the amount of characterization that could be obtained from a gradient reactor could possibly be improved if longer reactors and low programming rates were

used. It would then be possible to use heating methods other than a wire wound reactor, because high programming rates would not be needed. One possibility would be to use a low heat capacity furnace. Another possibility would be to use a quartz tube inside of a narrow wall stainless steel tube and heat the steel tube by direct electrical heating in the manner of Goforth (14). With either of these methods, it would be possible to monitor the heating rate continuously.

The use of flow controllers with micrometer settings and accurate flow meters would also enable the reproducibility of the results to be improved, since the flow rate could then be set more precisely and reproducibly. Another useful addition to the system would be a pressure gauge built into the gas lines ahead of the entrance to the pyrolyzer. The pressure in the pyrolyzer under actual operating conditions could then be easily determined and the flow rate calculated accurately.

A gradient reactor that is heated directly by an electric current can be easily automated since there are many devices readily available which can automatically program voltage. An automated gradient reactor would be extremely useful in a PGC system such as that shown in Figure 1.01. The reactor temperature could be programmed to the desired temperature and then lowered quickly to the initial value. This would enable several peaks to be pyrolyzed under the same conditions in quick succession. Combined with a fast analytical system and a file of fingerprints of known compounds, such a system

would make a good "poor man's mass spectrometer". In addition, automation for the programming rate would likely improve the reproducibility of the results since manual errors in timing the switching would be eliminated.

To design the best reactor for any pyrolysis it is necessary to know how certain basic variables affect the pyrolysis reaction. Such parameters as the size of the reactor chamber, the material of the reactor, and the kinetics of the reaction require additional clarification. The results from the Section 3.05 tend to indicate that the size of the reactor tubing, and the pressure and flow rate of the carrier gas may have a significant effect on the rate constant for the pyrolysis reaction. It would be necessary to compare the pyrolysis results of several materials (especially quartz and gold) under identical conditions and to determine the effects produced by each if meaningful results are to be obtained.

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APPENDIX

A.01 THE PYROLYSIS GAS CHROMATOGRAPHIC SYSTEM

A schematic diagram of the system is given in
Figure A.01

- A. Brooks flow controller
- B. Moore flow controller
- C. Matheson rotameter, model 642-B, Matheson of Canada, Whitby, Ontario
- D. Welmet Industries Limited type FDI01 furnace (for gold tubing reactor) - Welmet industries Limited, Welland, Ontario
- E. Pyrolyzer - See Chapter 2
- F. Air Bath
- G. Aerograph linear temperature programmer - Wilkins Instrument and Research Inc., Walnut Creek, California
- H. Porapak Q (Waters Associates, Framingham, Mass.) column 3 meters x 1/8 inch.
- I. Gow-Mac power supply, model 40-05-C, and Gow-Mac thermal conductivity cell - model 9285-D Gow-Mac Instrument Co., Madison, New Jersey
- J. Aerograph digital integrator - model 471-42- manufactured by Infotronics Corp., Houston, Texas
- K. Sargent recorder - model SR- E.H. Sargent and Co., Chicago, Illinois.
- L. Thermocouple readout - Assembly Products Inc. indicating pyrometer mounted with six switch selectable thermocouples - range 0-1100°C.

The helium carrier gas was used without purification, since purification by passing the helium through a molecular seive filled column, at liquid nitrogen temperature, made no noticeable difference in the level of impurities (determined by mass spectroscopy).

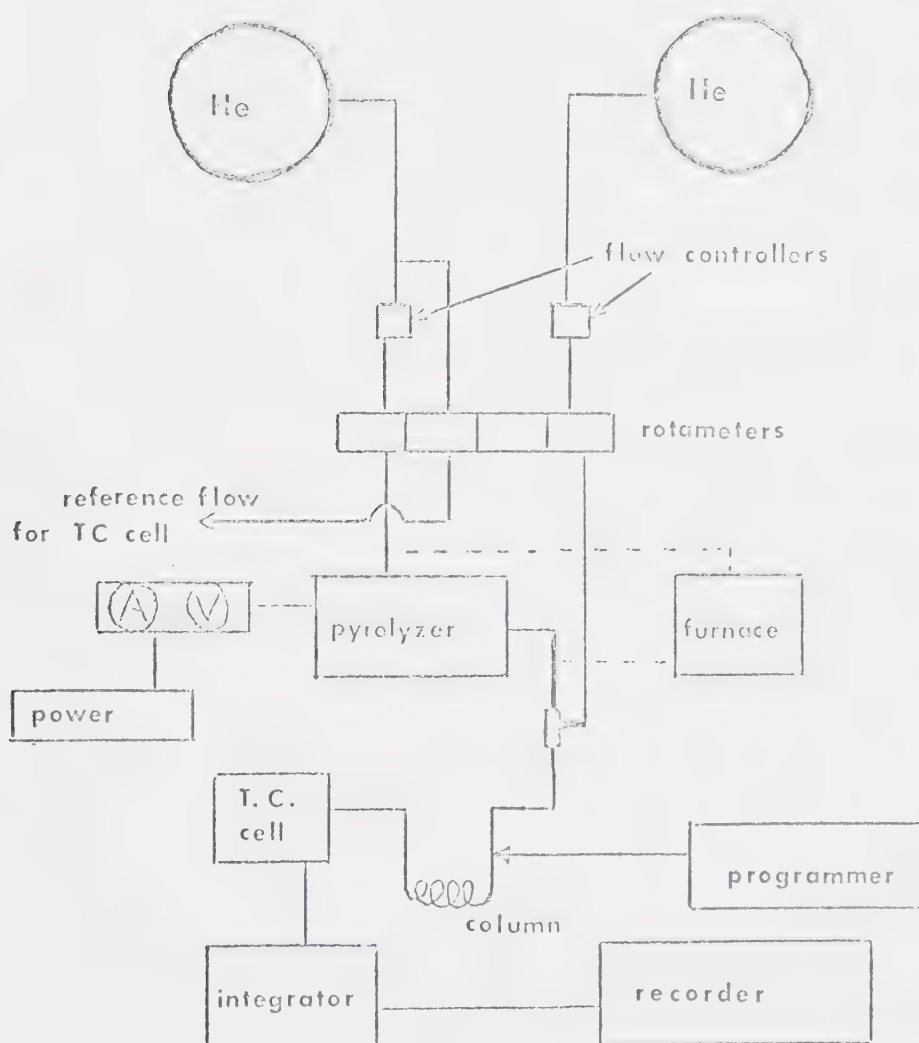


Figure A.01 Schematic diagram of the pyrolysis gas chromatographic system.

A.02 OPERATION OF THE SYSTEM

To facilitate the identification of the product peaks, the gas chromatograph was operated under "standardized" conditions. The column was maintained at $65 \pm 2^{\circ}\text{C}$ for approximately eight minutes (until ethane was eluted) and then programmed at five degrees per minute to 220°C . The temperature was then maintained at 220°C until all the peaks had been eluted(usually no more than five minutes after terminating programming). The power supply was operated at a bridge current of 200 milliamperes and a sensitivity of 900(out of 1000). The thermal conductivity cell was operated at a temperature of 230°C . The sample size used was 0.7 ± 0.1 microliter.

The product peaks were identified by comparing their retention temperatures to the retention temperatures of known mixtures chromatographed at the standardized conditions. It was found that the retention temperature of the hydrocarbon products varied almost linearly with the boiling point of a component for all components with molecular weights higher than propane. This relation was used as a rough guide to the identity of a component. The above method of identifying peaks does not result in an unambiguous identification because the column used was not efficient enough to resolve all the possible components. For example 1,3-butadiene was not differentiated from isobutylene and 1-butene. However, the method is adequate for the purposes of this study since it was not necessary to know the identity of all products.

Table A-1 shows the flow rate at the system outlet and the pressure in the pyrolysis unit as a function of the rotameter reading. The pressure was measured at the entrance to the pyrolyzer using a mercury manometer and the flow rate was measured at the system outlet using a soap bubble flow meter. The flow measurements were corrected to 0°C and 760mm of mercury. A graph of the results in Table A-1 (Figure A.02) was used to determine the pressure and the flow rate in the pyrolysis unit under operating conditions. The additive flow and the pyrolyzer flow were adjusted separately and then both turned on together, since then the readings on the rotameters were not reliable when both flow sources were used.

TABLE A-1 FLOW RATE AND PRESSURE AS A FUNCTION OF THE ROTAMETER READING(*)

<u>Rotameter</u>	<u>Pressure**(mm Hg)</u>	<u>Flow rate*** (ml/min)</u>
10 (1)	380	5.9
12 (2)	400	6.4
20 (1)	485	8.2
23 (2)	540	9.3
30 (2)	635	11.6
31 (1)	690	12.9
37 (2)	765	14.9
40 (1)	830	16.4
45 (2)	950	19.9

(1) additive flow (2) pyrolyzer flow

* All readings were taken at a tank pressure of 55 psig, atmospheric pressure of 699 mm Hg, room temperature 29°C, column temperature 65 \pm 2°C.

** pressure above atmospheric pressure

*** corrected to 0°C, 760 mm Hg, and for vapor pressure of water.

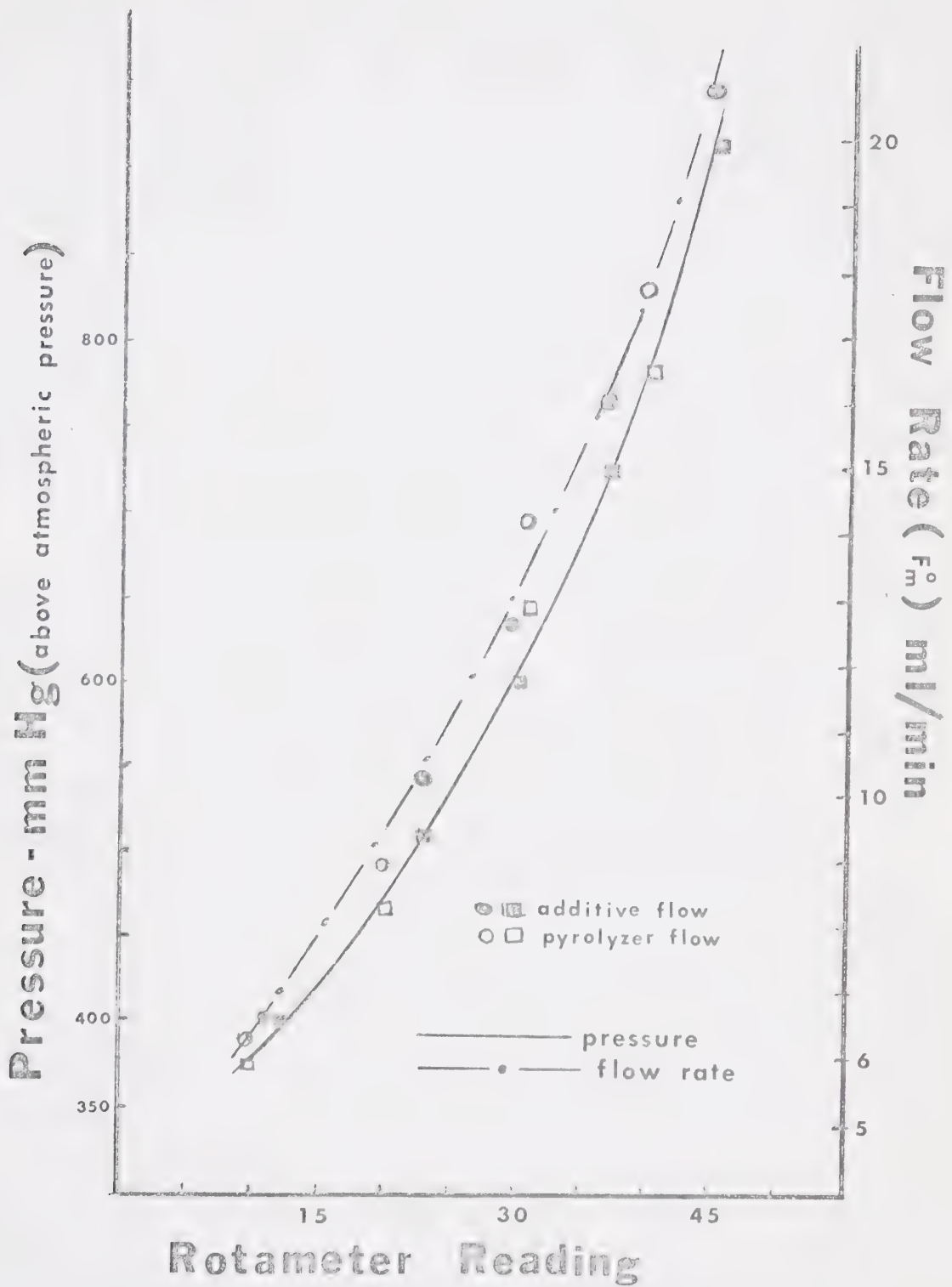
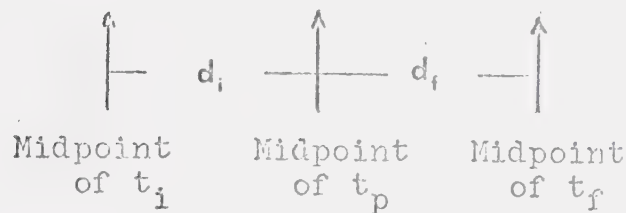
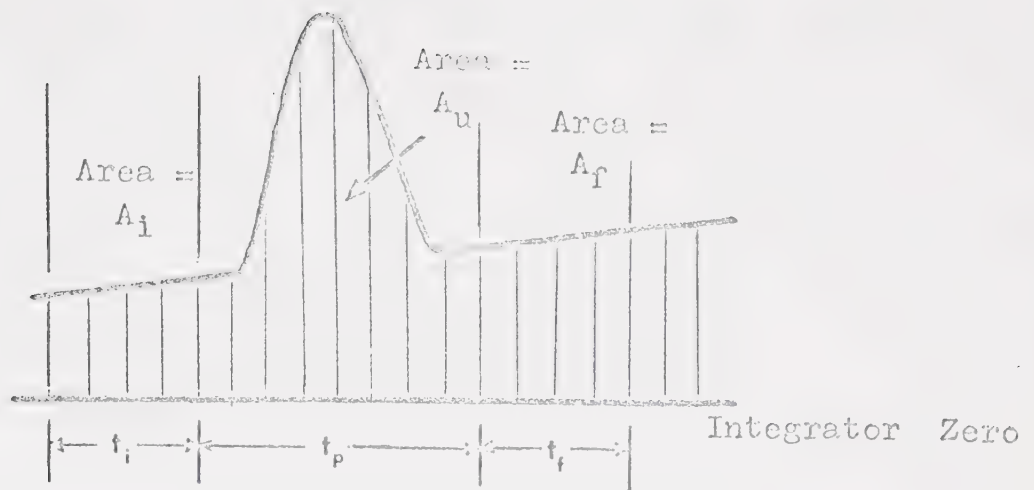


Figure A.02 Calibration of pressure in the pyrolyzer and the flowrate as a function of rotameter reading.

During the experimental work it was noticed that the peak areas obtained from the integrator were not reproducible, even though the pyrolysis conditions were reproduced accurately. This was especially noticeable for the smaller peaks, for which the areas varied widely even though the peaks appeared to be almost identical. The reason for this behavior is that the integrator peak sensing circuitry introduces error into the peak measurement which is critical with the smaller peaks. A review of various methods of measuring peak areas and the errors involved in each method is given by Johnson (16) and should be consulted for details.

To determine whether the errors in the peak areas affected the results significantly the method of sampling the peak at intervals described by Johnson was used. In this method the area of small intervals of the peak are measured and the total area calculated as illustrated in Figure A.03.

Equation A-1 is derived with the inherent assumption that the baseline is changing uniformly. When the formula could not be applied exactly because of overlapping peaks, it was assumed that the baseline changed uniformly and the valley between the peaks was used as a dividing line. That is, the area up to the peak valley was assumed to be the area of the first peak, and the area after the peak valley was assumed to be the area of the second peak. This assumption is reasonable if the peaks are approximately the same size and the amount of overlap is small. If the baseline was obviously non-uniform, attempts were made to



$$A_c = A_u - \frac{t_p}{d_i + d_f} \left(\frac{d_i A_f}{t_f} + \frac{d_f A_i}{t_i} \right) \quad (A-1)$$

where A_c = peak area corrected for baseline drift

A_u = sum of interval areas in time t_p (peak area before baseline correction)

A_i = sum of interval areas under segment of closest baseline preceding peak

A_f = sum of interval areas under segment of closest baseline following peak

t_i = width of segment for A_i , sec

t_f = width of segment for A_f , sec

t_p = width of segment for A_u , sec

d_i = time delay between midpoints of A_i and A_u (sec)

d_f = time delay between midpoints of A_u and A_f (sec)

Figure A.03 Calculation of peak area corrected for baseline drift.
(from Johnson(16))

approximate the varying slope by using different slopes for various intervals.

The areas that were obtained from the sampling technique were more reproducible than the areas obtained from the digital integrator alone, even though extensive approximation of the baseline was often necessary. However the gain in reproducibility of the small peaks was not considered worth the considerable time needed for calculating the areas of the peaks. In addition the areas of the major peaks were not changed significantly. It was therefore decided to operate the system using the areas printed out by the integrator in its regular mode -- this however, limits the precision with which the smaller peaks can be measured and may be a determining factor in lowering the reproducibility of the pyrolysis pattern.

The areas obtained from the integrator were converted to molar areas using the response factors given by Dietz (8). All calculations (unless otherwise specified) were based on the molar areas and not the peak areas since the molar ratios have more significance than area ratios. Using area ratios can change the appearance of the product distribution considerably (see Table A-2) and should be avoided.

A.03 STEPPED TEMPERATURE REACTOR

The residence times for the pyrolysis tubes designed to the specifications in Table 1 (Section 2.04) can be

calculated from the equation

$$\tau = \frac{\pi r^2 L T_o}{F_o T_p}$$

Assuming that $F_o = 10\text{ml/min}$ and $T_o = 300^\circ\text{K}$ the residence times for the pyrolysis tubes are:

$$P_1 \quad T_p = 410^\circ \text{C} \quad \tau = 6.0 \text{ sec}$$

$$P_2 \quad T_p = 490^\circ \text{C} \quad \tau = 5.9 \text{ sec}$$

$$P_3 \quad T_p = 560^\circ \text{C} \quad \tau = 5.9 \text{ sec}$$

$$P_4 \quad T_p = 630^\circ \text{C} \quad \tau = 5.9 \text{ sec}$$

TABLE A-2 COMPARISON OF PYROLYSIS PATTERN OF 2,3-dimethylbutane USING MOLAR AREAS AND PEAK AREAS

Products	Peak Area	Molar Area	Normalized peak area	Normalized peak molar area
methane	116,680	3270	99	100
ethylene	44,230	920	37	28
ethane	6,310	120	5	4
propylene +	123,250	1920	104*	59
isobutylene + 1,3-butadiene	39,510	490	33	15
trans + cis 2-butene	6,000	70	5	2
2-methyl-2- butene +	43,140	460	36	14
2,3-dimethyl butane	43,630	380	37	12
2,3-dimethyl- 2-butene	9,400	94	8	3
extent of reaction (α)		0.11		

* composed of propylene + propane; propylene = 100

When the pyrolysis tubes were constructed the lengths of the constant temperature zones and the flow rate were found to differ slightly from what was specified in Table 1, and the pyrolysis temperatures used differed considerably from the temperature specified. Some data for the temperature profiles can be seen in Tables A-3 to A-6 and graphs of this data are given in Figures A.04 and A.05. The actual measured flow (F_m^O) was 17 ml/min. From the pressure calibration (Figure A.02) the flow at the entrance to the pyrolyzer can be calculated as follows:

$$F_o = F_m^O \frac{p}{p_{py}} = 17 \frac{700}{1540} = 7.7 \text{ ml/min}$$

Table A-7 gives the actual residence times in the pyrolysis tubes at several temperatures. Values in Table A-7 marked with an asterisk are the values for which the reactor was originally designed. However, since few of the samples used were pyrolyzed significantly below 500°C the actual operating range of the reactor was 500 to 645°C. Some residence times for actual runs are given in Table A-8. It can be seen from Table A-8 that the times vary by about one to one and one-half seconds from the first pyrolysis tube to the last tube, with the last tube (the hottest tube) having the longest residence time. This is the opposite of what would be desired (the tube at the lowest temperature should have the longest residence time to obtain the best results) but the times differ so slightly that no attempt was made to correct this "fault".

TABLE A-3 TEMPERATURE READINGS* AS A FUNCTION OF DISTANCE
ALONG PYROLYSIS TUBE FOR PYROLYSIS TUBE P₁ (no flow)

Distance cm	Temp °C	Distance cm	Temp °C
1	230	15	525
2	405	16	520
3	480	17	520
* 4	510	18	525
5	520	19	520
6	525	20	520
7	530	21	515
8	540	22	520
9	535	23	515
10	535	* 24	515
11	530	25	505
12	530	26	470
13	530	27	260
14	530		

Median temperature =
525°C over constant
zone (*-*)
probable deviation 5°C
14/20 readings 525 ± 5°C
19/20 readings 525 ± 10°C
constant temperature
zone = 20 cm.

* Temperatures to nearest 5°C

TABLE A-4 TEMPERATURE READINGS* AS A FUNCTION OF DISTANCE
ALONG PYROLYSIS TUBE FOR PYROLYSIS TUBE P₂ (no flow)

Distance cm	Temp °C	Distance cm	Temp °C
1	390	15	595
2	540	16	595
* 3	585	17	590
4	590	18	590
5	595	19	585
6	600	20	585
7	595	21	580
8	600	22	570
9	595	23	580
10	590	24	590
11	590	25	590
12	590	* 26	580
13	590	27	555
14	590	28	330

Median temperature =
590°C over constant
zone(*-*)
probable deviation 5°C
18/20 readings 590 ± 5°C
Temperatures raised about
5°C when P₁ also on.
constant temperature
zone = 23 cm

* Temperatures to nearest 5°C

TABLE A-5 TEMPERATURE READINGS* AS A FUNCTION ON DISTANCE
ALONG PYROLYSIS TUBE FOR PYROLYSIS TUBE P₃(no flow)

Distance cm	Temp °C	Distance cm	Temp °C
1	250	16	570
2	500	17	570
3	555	18	580
* 4	560	19	575
5	570	20	575
6	575	21	575
7	570	22	580
8	570	23	575
9	575	24	575
10	580	25	575
11	580	26	575
12	580	27	570
13	580	* 28	575
14	575	29	530
15	570		

Median temperature =
575 over constant
zone(*-*)
probable deviation 5°C
all readings 575 ± 5°C
Temperature raised about
5°C when P₄ also on.
constant temperature
zone = 24.5 cm.

* Temperatures to nearest 5°C

TABLE A-6 TEMPERATURE READINGS* AS A FUNCTION OF DISTANCE
ALONG PYROLYSIS TUBE FOR PYROLYSIS TUBE P₄(no flow)

Distance cm	Temp °C	Distance cm	Temp °C
1	220	17	535
* 2	475	18	535
3	535	19	540
4	535	20	540
5	535	21	535
6	530	22	540
7	530	23	535
8	535	24	530
9	535	25	525
10	535	26	530
11	535	27	525
12	535	28	525
13	540	* 29	515
14	540	30	485
15	540	31	270
16	535		

Median temperature =
535 over constant
zone(*-*)
probable deviation 2.5°C
23/26 readings 535± 5°C
constant temperature
zone = 26 cm

* Temperatures to nearest 5°C

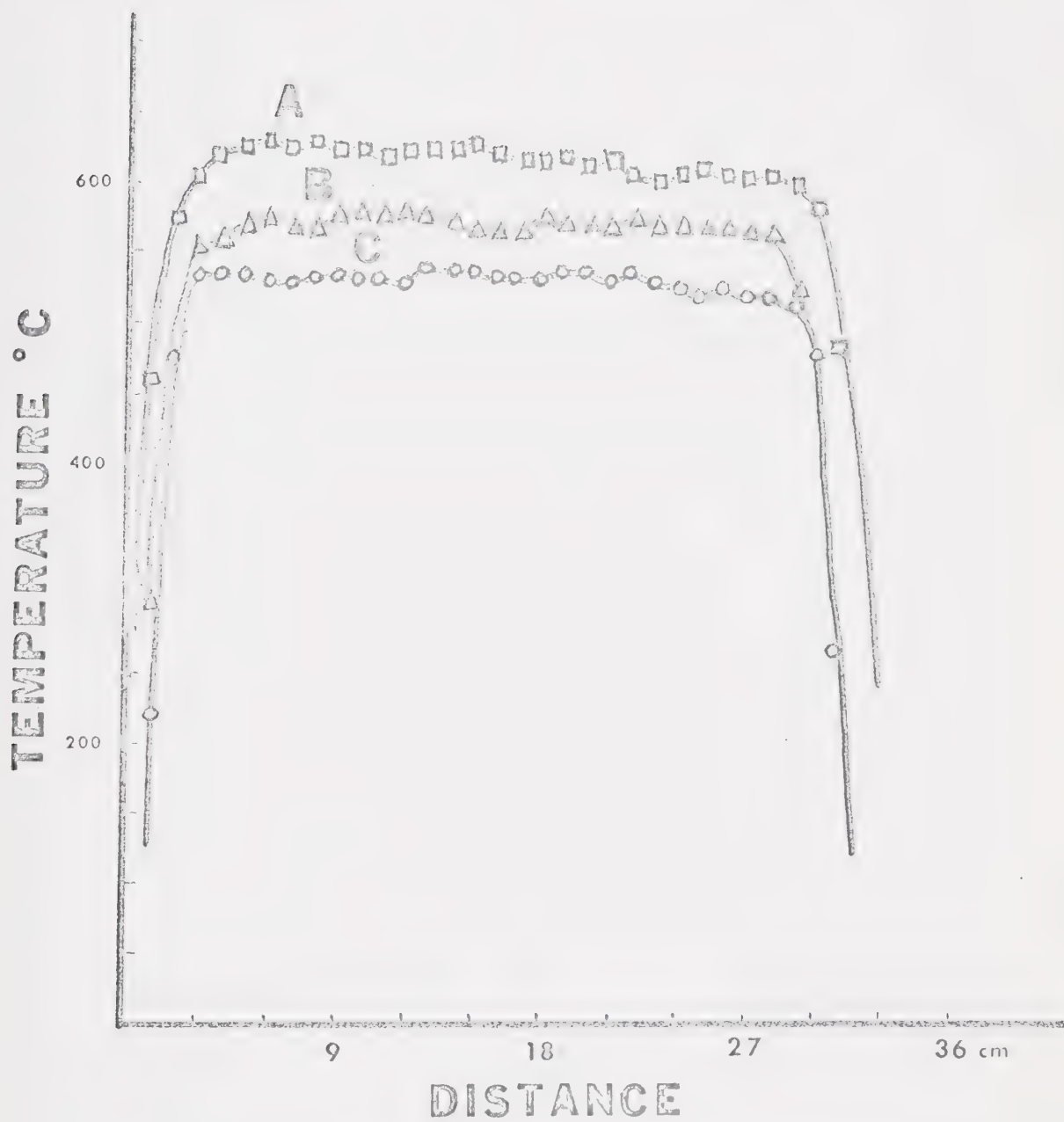


Figure A.04 Temperature profiles of pyrolyzer tubes. A. Pyrolysis tube P₄. B. Pyrolysis tube P₅. C. Pyrolysis tube P₄.

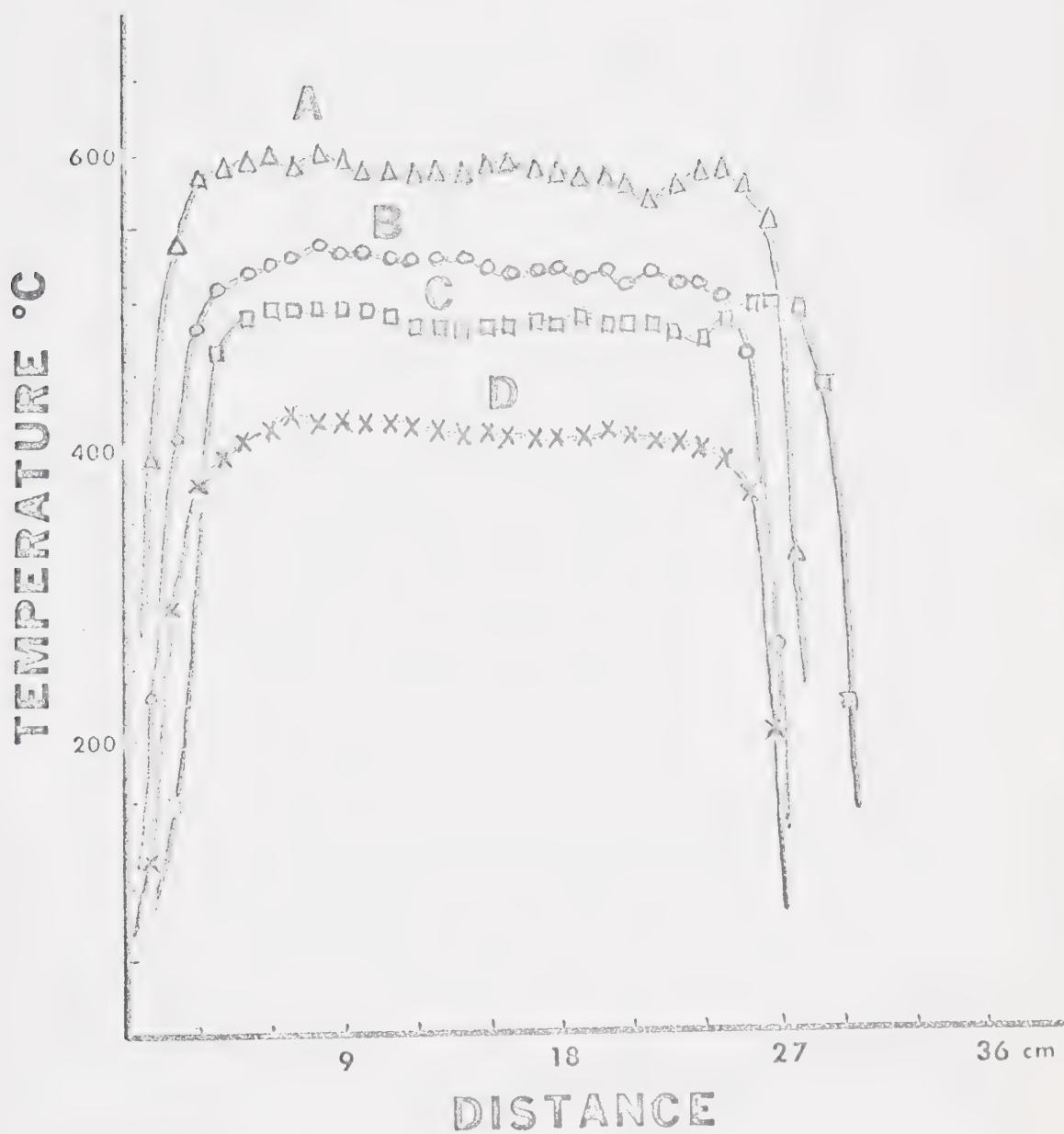


Figure A .05 Temperature profiles of pyrolysis tubes. A. Pyrolysis tube P₂. B. Pyrolysis tube P₁. C. Pyrolysis tube P₂. D. Pyrolysis tube P₁.

TABLE A-7 RESIDENCE TIMES FOR PYROLYSIS TUBES IN THE STEPPED TEMPERATURE REACTOR AT SEVERAL TEMPERATURES

Tube	Temp °C	τ sec	Tube	Temp °C	τ sec
P ₁	410*	7.1	P ₂	490	7.3
	500	6.3		530*	6.9
	550	5.9		580	6.5
	600	5.5		620	6.2
P ₃	530	7.4	P ₄	530	7.8
	560*	7.1		560	7.5
	600	5.5		630*	6.9
	620	6.6		640	6.9

TABLE A-8 RESIDENCE TIMES FOR PYROLYSIS TUBES IN THE STEPPED TEMPERATURE REACTOR IN SOME TYPICAL PYROLYSES

Tube	Temp °C	τ sec	Tube	Temp °C	τ sec
P ₁	535	6.0	P ₁	600	5.6
P ₂	560	6.6	P ₂	600	6.4
P ₃	595	6.7	P ₃	600	6.7
P ₄	620	7.0	P ₄	600	7.2

The diffusion coefficient can be calculated by the method of Chen and Other (5)

$$D_{12} = \frac{0.43 \left(\frac{T}{10} \right)^{1.75} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)^{0.5}}{p \left(\frac{T_{c1} T_{c2}}{10,000} \right)^{0.1405} \left[\left(\frac{V_{c1}}{100} \right)^{0.4} + \left(\frac{V_{c2}}{100} \right)^{0.4} \right]^2}$$

where D_{12} is the diffusion coefficient of 2 in 1, T is the temperature ($^{\circ}\text{K}$), p is the pressure in atmospheres, M_1 and M_2 are the masses of species 1 and 2, T_{c1} and T_{c2} are the critical temperatures of species 1 and 2, and V_{c1} and V_{c2} are the critical volumes of species 1 and 2.

For the diffusion coefficient of helium in helium ($D_{\text{He-He}}$)

$$T_{c1} = T_{c2} = 5.25^{\circ}\text{K}$$

$$M_1 = M_2 = 4.00$$

$$V_{c1} = V_{c2} = 5.76 \text{ cc/mole}$$

thus the diffusion coefficient of helium in helium can be evaluated

$${}^{298^{\circ}\text{K}}_{1 \text{ atm}} D_{\text{He-He}} = 1.95 \text{ cm}^2 \text{sec}^{-1}$$

$${}^{823^{\circ}\text{K}}_{2 \text{ atm}} D_{\text{He-He}} = 6.13 \text{ cm}^2 \text{sec}^{-1} \text{ (approximate pyrolysis conditions)}$$

$${}^{298^{\circ}\text{K}}_{2 \text{ atm}} D_{\text{He-He}} = 0.98 \text{ cm}^2 \text{sec}^{-1}$$

Benzene and normal hexane can be considered typical sample molecules. The diffusion coefficients of these

compounds are:

$$^{298^{\circ}\text{K}}_{1 \text{ atm}} D_{\text{He-benzene}} = 0.384 \text{ cm}^2 \text{ sec}^{-1} \quad (\text{from Giddings(13)})$$

$$^{298^{\circ}\text{K}}_{1 \text{ atm}} D_{\text{He-n-hexane}} = 0.313 \text{ cm}^2 \text{ sec}^{-1} \quad (\text{calculated from data of Giddings})$$

The diffusion coefficient at different temperatures and pressures can be calculated by realizing that the diffusion coefficient varies as $T^{1.81}$ and P^{-1} .

Using the results for the diffusion coefficient obtained above, the time taken for thermal equilibration can be calculated from the equation

$$t = \frac{0.019}{D}$$

At 298°K and two atmospheres pressure the time taken for thermal equilibration with helium diffusing is about 0.019 seconds. A sample molecule (n-hexane) under the same conditions requires about 0.12 seconds. At 550°C (823°K) the time for helium to diffuse to the wall of the tube (the thermal equilibration time) is about 0.003 seconds. n-Hexane under the same conditions requires 0.015 seconds.

The actual transition time is difficult to calculate because the temperature is increasing exponentially in the transition zone. However, an approximate value can be obtained by using the flow rate at the median temperature to calculate the time in the transition zone. Assuming the temperature in the transition zone increased from about 325°K (50°C) to about 850°K (580°C) the median temperature is about 590°K (315°C). The transition time for various

transition zone lengths can then be calculated using the following equation

$$t_z = \frac{\pi r^2 L T_o}{F_o T_{med}} = \frac{0.114}{7.7} \frac{273 L}{590}$$

where L is the length of the transition zone and T_{med} is the median temperature. The transition times for various lengths of transition zone then become:

$$\begin{aligned} \text{For } L &= 2.5 \text{ cm, } t_z = 1.0 \text{ sec} \\ &= 3.0 \text{ cm } = 1.2 \text{ sec} \\ &= 4.0 \text{ cm } = 1.6 \text{ sec} \end{aligned}$$

Assuming that an average residence time is approximately 6.5 seconds and an average transition time is about 1.3 seconds, then:

$$\frac{t_z}{\tau} = \frac{1.3}{6.5} = 0.20$$

This value for the ratio of transition time to the residence time is high. However the time the sample spends within ten percent of the pyrolysis temperature is the critical time (the time during which pyrolysis will occur), and this time would be considerably less than the total transition time. The high ratio of transition time to residence time must be considered to be a disadvantage of this type of reactor since extensive modifications would be required to decrease the transition time. The time required for thermal equilibration is small compared to the transition time and can be ignored.

A.04 TEMPERATURE GRADIENT REACTOR

Table A-9 shows some data for the change of temperature with time in the gradient reactor. Figure A-06 shows the plot of temperature as a function of time that was obtained for the temperature gradient reactor starting at an initial temperature of 500°C . The gradients obtained starting at an initial temperature of 450°C are given in Figure 2.18.

It was decided to operate the pyrolyzer with a pyrolysis time of about 15 seconds. This time is long enough to allow a considerable range of temperature to be obtained. The flow rate at the initial temperature required to obtain the desired pyrolysis time can be calculated from Equation 2-13. The flow rates required for a rate of

TABLE A-9 PROGRAM RATE AND TEMPERATURE AS A FUNCTION OF
WATTAGE APPLIED TO THE GRADIENT REACTOR

Initial temperature 450°C (130 watts)				Initial temperature 500°C (170 watts)			
W	ΔW	Temp	Rate	W	ΔW	Temp	Rate
314	184	517°C	4.5	316	146	550°C	3.3
340	210	519	4.6	356	186	570	4.7
382	252	539	5.9	400	230	580	5.3
438	308	555	7.0	445	275	600	6.7
473	343	585	9.0	475	305	615	7.7
516	386	585	9.0	520	350	625	8.3

W = wattage applied to the reactor
 ΔW = the difference in wattage applied and initial wattage
 Temp = the temperature attained in 15 seconds
 Rate = the program rate in degrees per second

9°C/second and T_0 of 450°C is 10.6 ml/min. For $R=8.3^\circ\text{C}/\text{sec}$ and $T_0 = 500^\circ\text{C}$ the flow required is 10.8 ml/min. These flow rates are at the initial temperature; if they are

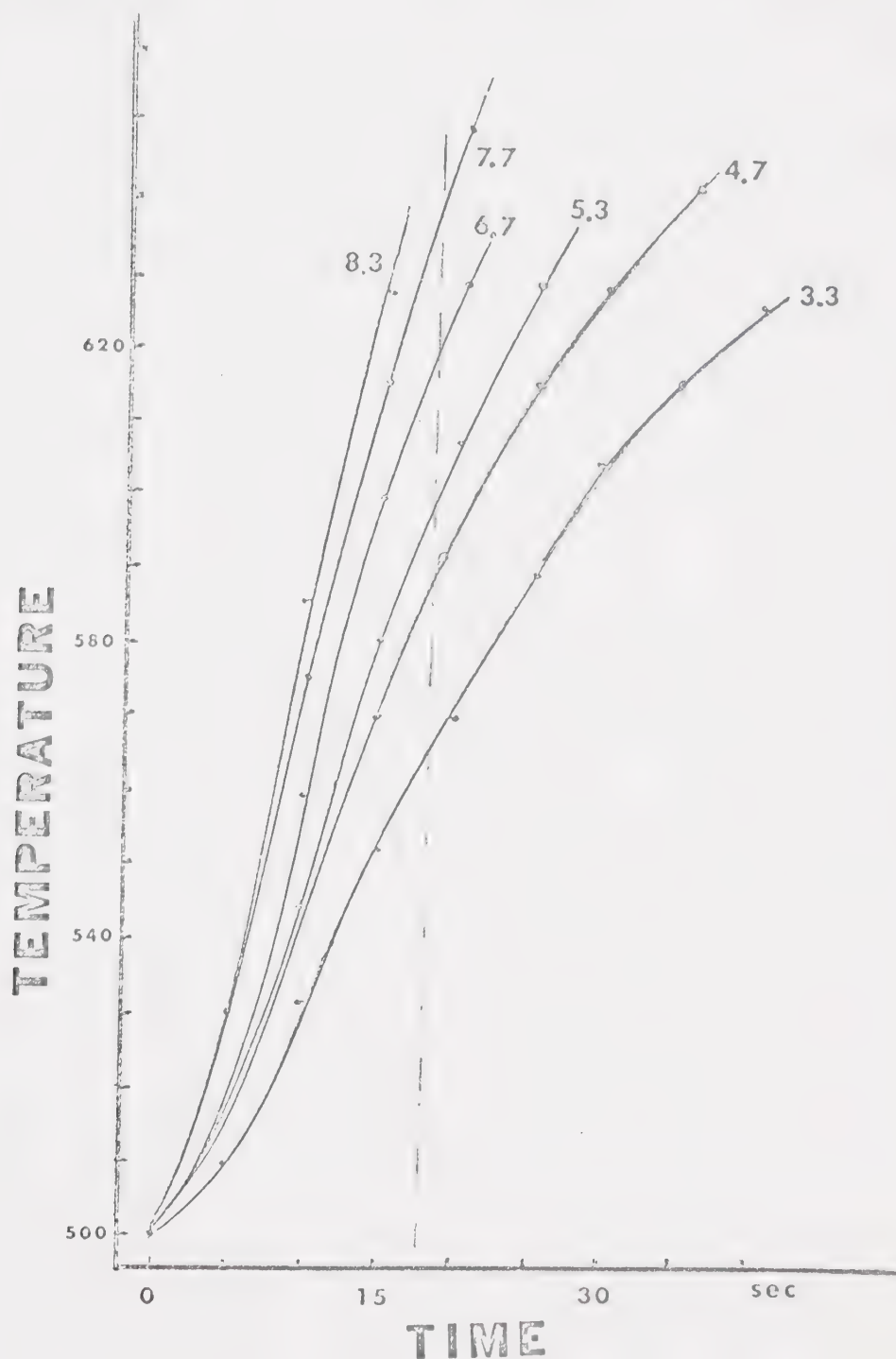


Figure A.06 Temperature gradients obtained from the gradient reactor starting at an initial temperature of 500°C. Numbers on the graph are the programming rates in degrees Centigrade per second.

corrected to 0°C they become

$$273^{\circ}\text{K}_{\text{F}_0} \text{ (for } T_0 = 450^{\circ}\text{C) } = 4.0 \text{ ml/min}$$

$$273^{\circ}\text{K}_{\text{F}_0} \text{ (for } T_0 = 500^{\circ}\text{C) } = 3.8 \text{ ml/min}$$

These are extremely low rates and are difficult to control precisely.

The actual flow rate(F_m^0) under operating conditions was 8.2 ml/min(with F_{py} operating only). The flow setting of the system were $\text{F}_{\text{py}} = 20$, $\text{F}_{\text{add}} = 23$ and the total pressure 1700 mm Hg. The actual flow rate at the entrance to the pyrolyzer can thus be calculated as $\text{F}_0 = 3.7 \text{ ml/min}$. The pyrolysis time that would result from this flow can be calculated from Equation 2-14. For $T_0 = 500^{\circ}\text{C}$ (773°K) and $R = 8.3^{\circ}/\text{sec}$ the pyrolysis time (t_p) is 15.6 seconds. Table A-10 shows the pyrolysis times obtained for an initial temperature of 450°C and various program rates. As can be seen the pyrolysis in time increases as the rate decreases. The pyrolysis time that would result if the flow rate were

TABLE A-10 VARIATION IN PYROLYSIS TIME WITH PROGRAMMING RATE AND FLOW RATE

$T_0 = 450^{\circ}\text{C}$ $\text{F}_0 = 3.7 \text{ ml/min}$		$T_0 = 450^{\circ}\text{C}$ $\text{F}_0 = 3.3 \text{ ml/min}$	
$R \text{ }^{\circ}\text{C/sec}$	$t_p \text{ sec}$	$R \text{ }^{\circ}\text{C/sec}$	$t_p \text{ sec}$
9.0	16.4	9.0	18.1
7.0	16.7	7.0	18.3
5.9	16.9	5.9	18.7
4.6	17.1	4.6	18.9

decreased by ten percent is also shown. It is apparent that a considerable error can be introduced into the temperature range (and the final temperature) if the flow changes. The minimum error caused by flow changes of ten percent is about eight degrees centigrade. However a change of even this amount can result in a considerable change in extent of pyrolysis. When it is considered that a ten percent change in the flow rate is only about 0.4 ml/min and controlling the flow with the precision is extremely difficult, it can be seen that the errors in the temperature range could be relatively large. The pyrolysis times and the temperature ranges quoted are thus only approximate.

A.05 GOLD TUBING REACTOR

For the purpose of comparison with the results obtained from quartz tubing, two pyrolysis tubes made from gold were constructed. The tubes were heated in a small furnace and the temperature measured by placing a thermocouple into the furnace cavity. Figure A.07 shows the general construction of the pyrolysis tubes.

A.05-1 3 mm diameter Gold Tubing

Specifications:

inside diameter	-	3 mm
wall thickness	-	0.025 inch
length 99 cm.	-	97 cm inside pyrolyzer
Volume of constant temperature zone	-	6.85 cm ³

Coil wound into
spiral 3 cm. in diameter
and 5 cm high (see Figure
A.07).

Because of the large volume of the reactor it was necessary to use high flow rates to obtain pyrolysis times of ten to twenty seconds. Pyrolysis times of less than ten seconds were not obtained. To obtain times of less than ten seconds the experimental apparatus would have to be modified extensively.

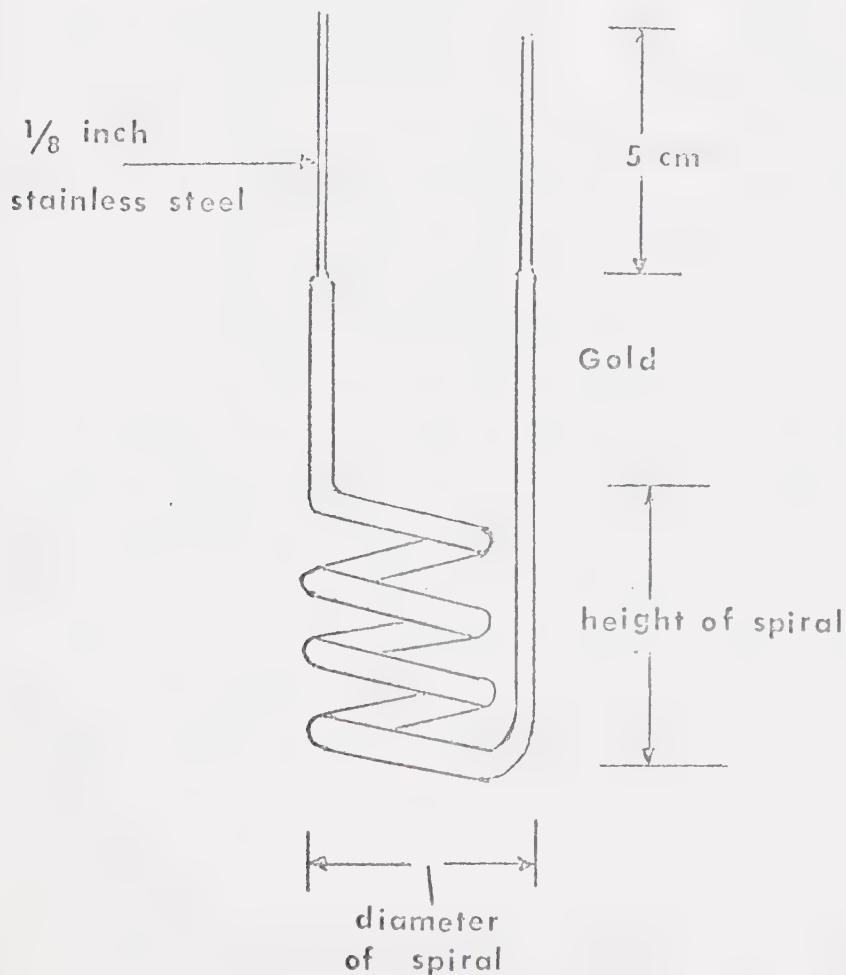


Figure A.07 General construction of the gold tubing reactors.

Under operating conditions;

$F_{py} = 19.9$ ml/min, total pressure = 1650 mm Hg
thereofre $F_o = 9.2$ ml/min. Table 15 (Section 3.05) gives the residence times that result from this flow rate at various temperatures. No effort was made to adjust the flow rate so that the residence times were equal because it had been previously found that making small corrections in the flow rate was difficult, and excessively time consuming.

A.05-2 1 mm diameter Gold Tubing

Specifications:

inside diameter	1 mm
wall thickness	0.020 inch
length 100 cm	95 cm inside pyrolyzer
Volume of constant temperature zone	0.75 cm ³
Coil wound into spiral 3 cm in diameter and 3 cm high (see Figure A-07)	

Because of the extremely small volume of the reactor made from the 1 mm diameter gold tubing, it was not possible to obtain residence times longer than seven seconds without modifying the system. To obtain a pyrolysis time of about six seconds the reactor had to be operated at low flow rates. The operating conditions were: $F_{py} = 6$ ml/min

$$F_{add} = 11.8 \text{ ml/min}$$

$$\text{total pressure} = 1735 \text{ mm. Hg}$$

The flow rate at the entrance to the pyrolyzer can thus be calculated as $F_o = 2.6$ ml/min. The residence times that resulted from this flow rate at various temperatures are given in Table 15 (Section 3.05).

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